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Volume 5, Part 5

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Hardy Vincent Ellsworth

1889–1952

THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 38 MAY-JUNE 1953 Nos. 5 and 6

MEMORIAL OF HARDY VINCENT ELLSWORTH

MAURICE HAYCOCK, *Ottawa, Canada.*

The death of Hardy Vincent Ellsworth on October 4, 1952, came as an unexpected shock to his many friends and colleagues throughout Canada and the United States. He entered hospital, for the first time in his life, on September 10, 1952, and underwent an operation from which he appeared to be making a recovery. However, on October 4 his condition suddenly became acute and he passed away mercifully quickly. For some years he had been forced to restrict active field work with the Geological Survey of Canada because of signs of heart weakness, but he nevertheless devoted himself assiduously to his work in the laboratory. Under a heavy load because of the demand for his services in the field of radioactive raw materials he still maintained satisfactory health until shortly before his hospitalization.

Ellsworth was born at Ridgeway, Ontario, on September 1, 1889. While he was the only son of Walter E. Ellsworth and Catharine Barnhard, he was the youngest of a family of five children, the others by a former marriage. His father was an influential and prosperous farmer who took a leading part in the life of the community, but who died when the son was two years old. He was brought up by his grandmother and received his early education at Ridgeway and Welland, Ontario. In the autumn of 1909 he registered at University College of the University of Toronto and graduated with the class of 1913. Under fellowships he continued for the next three years with post-graduate studies receiving his M.A. in 1914 and his Ph.D. in 1916. Rejected for war service because of his physique, he remained at the university for still another year as demonstrator in electrochemistry. In 1918 he was appointed mineralogist with the Geological Survey of Canada, a position which he filled with growing distinction until his death. In 1928 he was married to Mabel C. Adams with whom he had many common interests and by whom he is survived.

Ellsworth was widely known as a brilliant classical mineralogist and as a chemist whose craftsmanship and accuracy were of rare excellence. Very early his interest was focused on the rare earth and radioactive group of minerals and in 1922 the first of many contributions in this field was published. Later his comprehensive memoir "Rare Element Minerals of Canada" quickly became, and still remains, a classic. His interest grew and it was natural that it should be directed toward the use of atomic disintegration as a measure of geologic time. He became an original member of the Committee on the Measurement of Geological Time of the United States National Research Council under the chairmanship of the late A. C. Lane. It was Ellsworth who carried out the analyses which established the age of the oldest known rocks as two billion years. In his early field work on the radioactive pegmatites Ellsworth had used an electroscope for detecting radioactivity. When Messrs. Shrum and Smith in 1934 described a Geiger counter which weighed some 55 pounds he was quick to see its possibilities in the field. He built one weighing 21 pounds. Much later it was he who suggested the design of a pocket model using hearing-aid batteries and miniature tubes.

With the soaring of the radioactive elements into acute world importance, Ellsworth was prepared by long experience to make major contributions. He became head of and organized the laboratory of the Radioactive Division of the Geological Survey of Canada, which is the official agency of the Atomic Energy Control Board for matters dealing with private prospectors and mining companies. He also found time to be one of the most active members and chairman of the Canadian group of the Joint Committee on Mineralogical Research of the Radioactive Minerals set up by Canadian and United States atomic energy authorities.

It was inevitable that high honours should come to one with such a record of experience and devotion to service, although personally, Ellsworth was always inclined to withdraw modestly from publicity. He was a member of the American Chemical Society and of the Canadian Institute of Mining and Metallurgy. He was a Fellow of the Mineralogical Society of America and in 1937 served as Vice-President. In 1952 he was again elected Vice-President (for 1953). He was a Fellow of the Mineralogical Society of Great Britain and Ireland (London). In 1949 he was awarded the Willet G. Miller medal of the Royal Society of Canada in recognition of his contributions. Modest and unassuming, he possessed rare vision and an active imagination. He was repeatedly advancing new ideas, many of which he himself regarded with humour, but some paid off handsomely. This originality of imagination is possible only in one who has varied active interests, and it was so in his case. Few of his associates were aware of his versatility because of his reluctance to talk about his own accomplishments.

Ellsworth, known as "H. V." from his student days, was primarily interested in mineralogy. He built up a personal collection of rare and unusually fine specimens, the quality of which is in inverse proportion to its relatively small size. At one period he engaged in the grinding and polishing of gem stones. Always an avid reader, he amassed a considerable library which contains not only scientific books but also the classics; many of his books are collectors' items. Much of his spare time during the summers was devoted to his garden and it was only natural that here he carried on experiments. A miniature rail fence, examples of which are now being replaced with less lovely enclosures, along which grow tiny elms can still be seen. The fence is the work of Mrs. Ellsworth, the stunted elms are a product of his experiments. His love for the beautiful is everywhere apparent in his home. His collections of pottery, oil and water-colour paintings and carved wood pieces testify to his artistic taste. Although few people are aware of the fact, both he and Mrs. Ellsworth played violins for their own enjoyment; both studied art during one winter. He enjoyed good music and had a large collection of classical recordings. At another time he took up wood carving, for he loved to work with wood. He re-built his fireplace and made and finished all of the woodwork of his living-room. He even had a small machine shop in his home, and many small experimental gadgets found their way from this shop to instruments in his laboratory. Another hobby was that of photography in which he indulged on his field trips. One cannot escape the feeling that he was one who would tackle any project which sufficiently captured his interest, regardless of difficulties. He was a perfectionist at heart and, as is so often the case with perfectionists, his achievements fell so far short of his ideals that he said little even to his close associates.

Of Ellsworth the University College year-book for 1913 states in part "his greatest ambition is to bear a part in developing the natural resources of our fair Dominion." His works will testify that he has realized his early ambition with great distinction, and his loss to the ranks of mineralogists in this country and others will long be felt.

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SPHERULITIC ALKALI RHYOLITE DIKES IN THE ATSUTLA RANGE, NORTHERN BRITISH COLUMBIA[1]

W. H. MATHEWS, *University of British Columbia, Vancouver*

AND

K. D. WATSON, *University of California, Los Angeles.*

ABSTRACT

Several alkali rhyolite dikes, generally displaying spherulitic structure, and containing riebeckite, acmite, or decomposition products of riebeckite, occur in the Atsutla Range of northern British Columbia. Spherulitic growth in one dike has been initiated at the corners or edges of phenocrysts; axiolitic growth in another dike has taken place from surfaces of contorted flow layers; elsewhere, the features that have localized spherulitic growth are not apparent. Where both the dark and felsic minerals show radial growth in the same dike, the centers of crystallization of these two groups of minerals are either separate or shared. Mechanical rejection of acmite and riebeckite by quartz but not by potash feldspar is offered as an explanation for clear crescentic masses of quartz exposed in sections of cloudy feldspathic spherulites.

Acmite crystallized before riebeckite in part of one dike, but riebeckite has been pseudomorphed by acmite in a neighboring part of the same dike. Minor and local variations in temperature or pressure may explain this reversal in sequence of crystallization. Analyses of two dikes show zirconia exceeding 0.4%. Zircon occurs with mixtures of black opaque grains, goethite, and hematite that are pseudomorphous after riebeckite but not with this mineral in its unaltered state. Riebeckite, therefore, and possibly acmite as well, may contain appreciable amounts of zirconia in solid solution.

GEOLOGICAL SETTING

The southeastern part of the Atsutla Range of northern British Columbia (Fig. 1) is composed of granitic rocks of the Glundebery batholith which intrude sedimentary and volcanic rocks of Permian and Lower Mesozoic age exposed on the margins of the range (Watson & Mathews, 1944). The Glundebery batholith is made up mainly of granite and quartz monzonite but it also consists of minor amounts of granodiorite, quartz diorite, syenite, diorite, and gabbro. A stock of miarolitic micrographic granite is present in the central part of the batholith and may be one of the latest phases of the intrusion. The rhyolite dikes discussed in this paper, which are partly spherulitic and riebeckite- or riebeckite and acmite-bearing, occur in and adjacent to the batholith.

One dike cuts typical granitic rock in the central part of the batholith on the north fork of Nazcha Creek (locality A, Fig. 2). This dike, which is dark greenish grey and aphanitic, has a width of 3 feet, a vertical dip, and an exposed length of about 20 feet. Its margins have closely-spaced

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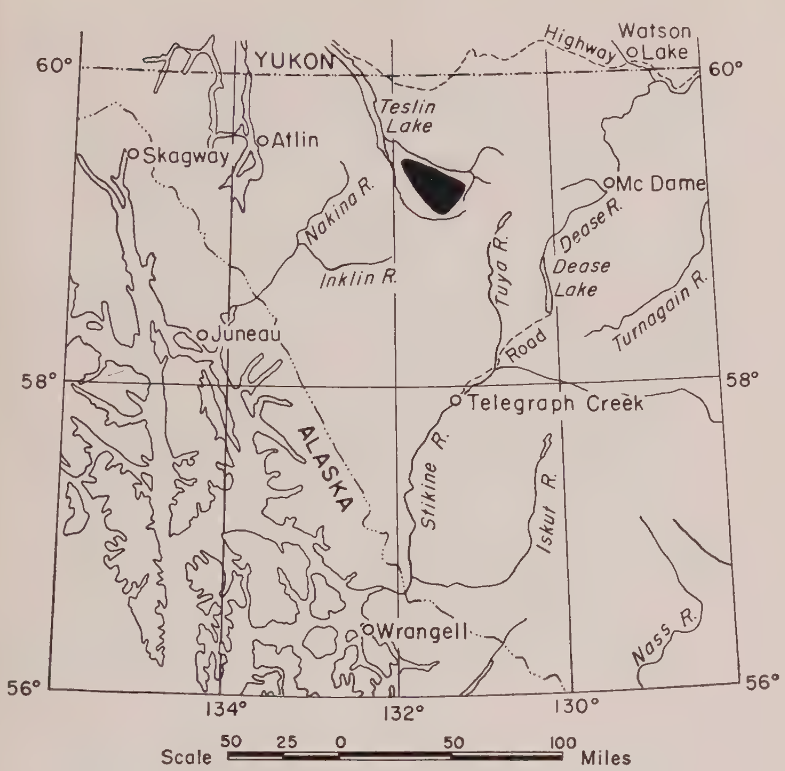


FIG. 1. Key-map of northern British Columbia showing (in black) location of Atsutla Range.

flow layers parallel to the walls; a few inches toward the center of the dike the flow layers are distinctly contorted. These zones of contorted flow layers grade, in turn, into a central zone marked by discrete to coalescent dark blue to almost black spherulites, 3 to 5 mm. in diameter. The flow layers become progressively less distinct toward the center of the zone and in places are marked only by lines of spherulites.

Fragments of similar rhyolite were found in talus at two localities, one near the southern contact of the batholith, and one near its northeastern limit.

Several dikes, which are moderately to steeply dipping and up to 20 feet wide, cut the wall rocks of the Glundebery batholith on the west side of Glundebery Valley (locality B, Fig. 2). These dikes have pale grey finely crystalline cores and white to buff microcrystalline margins that contain more or less well defined dark fibrous spherulites up to 6 mm. in diameter.

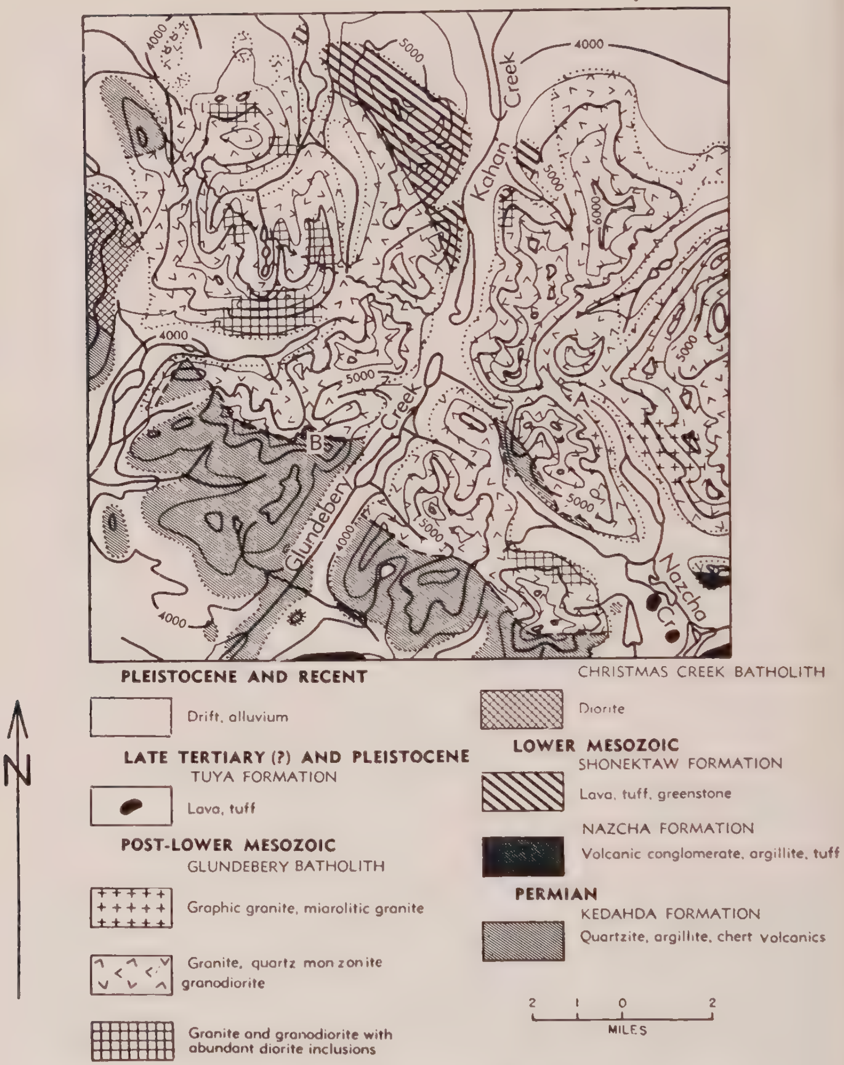


Fig. 2. Geological map of part of the Atsutla Range showing localities (A and B) at which rhyolite dikes are present.

Mineralogy

Phenocrysts were seen in a conspicuously spherulitic zone in one of the Glundebery Valley dikes but not elsewhere. They consist of euhedral to highly corroded quartz grains of β habit up to 0.5 mm. in diameter, and euhedral feldspar crystals up to 1.5 mm. long, composed of fine grid-like microperthitic intergrowths of potash and soda feldspar (Fig.

3–5). The feldspar phenocrysts are markedly similar to those in the groundmass of much of the granite of the Glundebery batholith.

The minerals composing the non-porphyritic dikes and the groundmass of the porphyritic one are quartz, potash and plagioclase feldspars, riebeckite, acmite, zircon, black opaque grains, goethite, hematite, and sericite (?).

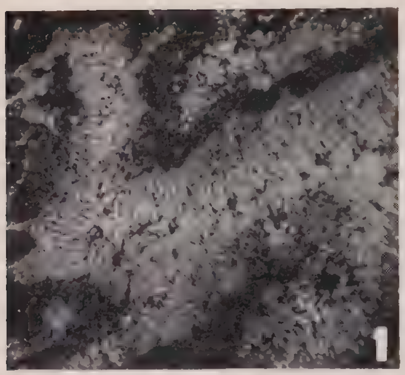
Feldspars. Where the feldspars are fine-grained and clouded with minute impurities, stain tests (after Keith, 1939, and Chayes, 1952) had to be used to distinguish the potash-rich and plagioclase-rich areas. As shown by the chemical analyses (Table 1), little or no calcium is available for anorthite and the plagioclase, therefore, approximates pure albite. The optical properties of the plagioclase in the coarser non-spherulitic rhyolite indicate this same composition.

Riebeckite. The riebeckite forms stout to acicular prisms with parallel extinction, negative elongation, low birefringence, and refractive indices of about 1.68. The pleochroism is distinct with X dark blue; Y yellow green; and Z pale yellow. The needles show well-defined amphibole cross-sections. Some needles in the spherulites of the Nazcha Valley dike cannot be identified with certainty because of their exceedingly small size, but they show the same pleochroism as riebeckite found elsewhere in the dike. Evidence presented later in this paper suggests that the riebeckite, as well as acmite, may contain zirconium.

One of the two common alteration products of the riebeckite is a pale yellowish pseudomorph with distinctly higher birefringence but the same parallel extinction and negative elongation. Scattered needles of riebeckite within a single bundle may be replaced by this yellowish mineral and adjacent needles may remain completely unaltered. A few needles are composed of riebeckite at the base and of the yellowish mineral at the distal end, the two parts being separated by a clearly defined boundary cutting obliquely across the crystal. This alteration product has been identified tentatively as acmite.

A second alteration product of riebeckite, present in the Glundebery Valley dikes, is a mixture of black opaque grains, goethite, and hematite, with closely associated zircon. In a few fibers, some of the pleochroic amphibole is preserved. Some riebeckite needles within a single spherulite show this alteration while others remain completely unaltered. In the slightly spherulitic rhyolite, fiber-like trains of black opaque grains and hematite are assumed to represent former riebeckite needles.

Acmite. Acmite occurs chiefly as small equant grains and stout prisms disseminated throughout the spherulites of the Nazcha Valley dike and it is also present as stout radiating fibers in a few interspherulitic parts of this rock. It has pale yellow color, scarcely noticeable pleochroism, high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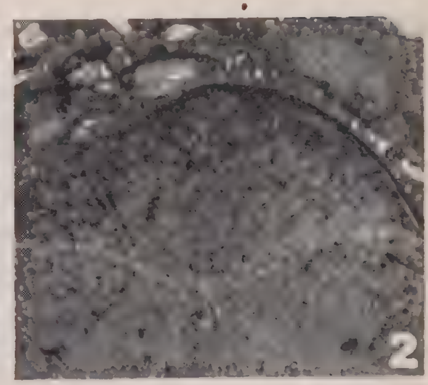
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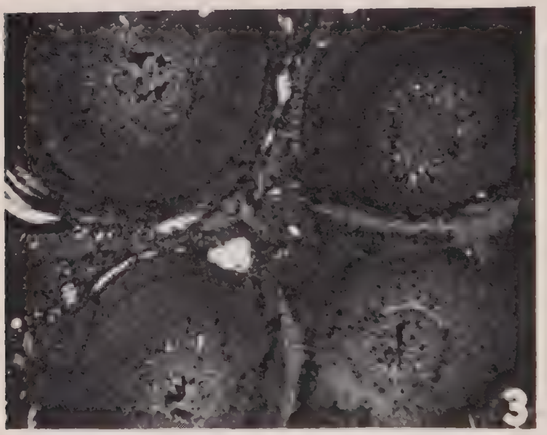
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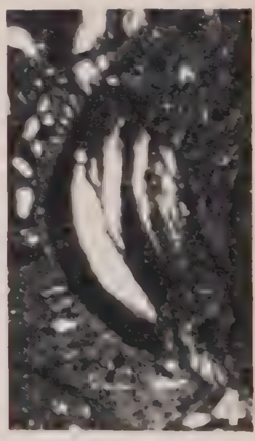
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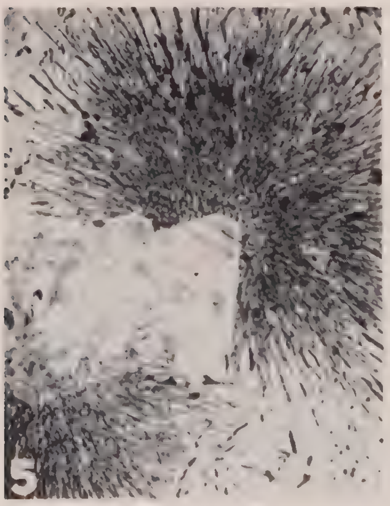
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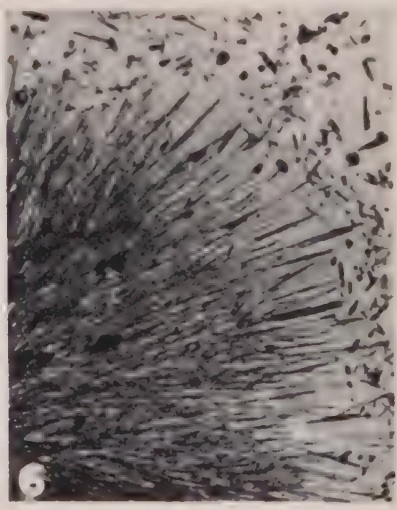
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birefringence, and refractive indices ranging from 1.76 to more than 1.79. The prisms have negative elongation and parallel extinction. Although the indices of the acmite (?) psuedomorphous after riebeckite have not been determined, its other optical properties correspond to those given above.

Zircon. Zircon occurs as fine crystals adjacent to the black opaque grains, goethite, and hematite after riebeckite but it was not seen in the vicinity of unaltered riebeckite.

Black Opaque Minerals, Goethite, and Hematite. Black opaque grains, goethite, and hematite are common as alteration products of riebeckite needles. In one section of non-spherulitic rhyolite, however, black opaque grains and goethite occur together as interstitial grains up to 0.4 mm. in diameter making up about 5 per cent of the rock and distributed fairly uniformly throughout it. *X*-ray analyses of magnetic concentrates show that the magnetite content of the three analyzed rocks is less than 0.17, 0.10, and 0.04 per cent respectively.[1]

PETROGRAPHY

Feldspathic Spherulites of the Nazcha Valley Dike

Feldspathic spherulites are well developed only in the central part of the Nazcha Valley dike (locality A, Fig. 2). They are clearly distinct from spherulites or axiolites composed of radiating fibers of riebeckite which occur not only in the Glundebery Valley dikes but also locally in the margins of the Nazcha Valley dike. These feldspathic spherulites display several concentric zones with fairly distinct structure and mineral

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[1] Chief Analyst and Assayer, B. C. Department of Mines. Personal communication, February 7, 1947.

FIG. 3-1. Contorted flow layers in Nazcha Valley dike. Layers of cloudy, finely-crystalline riebeckite and potash feldspar alternating with more coarsely-crystalline quartz and riebeckite needles. ×15.

FIG. 3-2. Secondarily branching fibers of potash feldspar at outer edge of second zone of feldspathic spherulite in Nazcha Valley dike. ×40.

FIG. 3-3. Closely packed feldspathic spherulites in central part of Nazcha Valley dike. Clear crescentic areas are composed of radiating fibers of quartz and minor plagioclase. ×15.

FIG. 3-4. Clear crescentic areas composed of fibers of quartz and minor plagioclase with acmite-rich rims on their convex surfaces. Nazcha Valley dike. ×40.

FIG. 3-5. Riebeckite needles and pseudomorphs after riebeckite radiating from corners or edges of microperthite phenocryst. Glundebery Valley. ×25.

FIG. 3-6. Rim of spherulite showing ends of radially-arranged needles of riebeckite and tangentially-arranged stouter prisms of riebeckite in quartz and potash feldspar. Glundebery Valley. ×40.

content (Fig. 3-3). Where the spherulites are widely spaced, all zones may be present, but where they are closely packed, only the innermost two or three zones are developed. The successive zones, from the center of the spherulites outward are as follows:

First (Innermost) Zone. This relatively clear zone has an ill-defined roughly polygonal to circular outline with a radius of 0.25 to 0.45 mm. It is made up of irregular grains of potash-rich feldspar containing abundant clusters of minute elongate grains of acmite and, around the margins of the zone, a few prisms of riebeckite.

The acmite granules range from 2 to 10 μ in length in the center of the zone but are 10 to 15 μ long toward the margins; the riebeckite prisms reach 10 by 30 μ.

Second Zone. This zone, 0.60 to 1.25 mm. in width, is composed of radial fibrous growths of potash-rich feldspar containing scattered granules of acmite and a felted mass of minute needles having the pleochroism of riebeckite.

The acmite has a fairly uniform grain size throughout the zone. The riebeckite (?) needles, on the other hand, which average about 5 μ in length at the inner edge of the zone, become progressively smaller toward the outer edge where they average 1 to 2 μ in length, and merge into a general cloudiness characteristic of the outer zones. The inner limit of the felted mass of needles lies at the polygonal to circular border of the innermost zone and corresponds approximately to the inner limit of fibrous feldspar. Stain tests show that the matrix of the second zone is composed chiefly of potash feldspar, although some narrow sectors may be composed of plagioclase feldspar and quartz. The fibers have parallel or slightly oblique extinction and may have either positive or negative elongation. Rare sectors of secondarily branching fibers similar in form to those described and illustrated by Iddings (1891, p. 458 and Fig. 6) are present. These secondary branches apparently grew faster than or developed in advance of the primary fibers, for in their sectors the fine regular cloudy growth line that marks the outer limit of this zone is bowed outward (Fig. 3–2). Elsewhere, this growth line is nearly circular.

Third Zone. This zone, which reaches 0.70 mm. in width, consists mainly of potash feldspar clouded with submicroscopic crystallites of riebeckite (?) and widely scattered grains of acmite. The acmite in the matrix of this zone forms granules up to 20 μ in diameter. Radiating fibrous growth is shown by the potash feldspar though it is less well-developed than in the two adjacent zones.

The third zone is characterized in section by numerous clear crescentic areas reaching dimensions of 2.5 by 0.6 mm., composed of radiating fibers of quartz and minor plagioclase, and rather sharply defined from the cloudy groundmass. Almost all of these areas are concave toward the center of the spherulite, their inner edges being concentric with or more sharply curved than the growth line marking the inner edge of the third zone. Some irregularities in their shape may be attributed to partial merging of adjacent crescents. The crescents are not uniformly distributed but are as a rule least common where spherulites are most closely packed.

The quartz fibers of the crescents show a strong preferred orientation with both their greatest lengths and optic axes normal to the inner walls of the crescents. Acmite, which is about uniformly distributed throughout the surrounding cloudy feldspathic groundmass, is absent from the central part of the clear crescents, but is concentrated in a narrow rim on their outer convex surfaces. The width of the acmite-rich rim in any sector of the crescent is roughly proportional to the width of the crescent, and approximately the same amount of acmite is present in any one sector as in an equal area of the adjacent cloudy matrix. The submicroscopic riebeckite (?), like the acmite, is concentrated on the outer surfaces of the crescents where it forms a dark rim approximately equal to the width of the crescent and about twice as cloudy as the surrounding feldspathic matrix.

With few exceptions the crescents lie in the third zone outside the fine cloudy circular line marking the outer limit of the second zone. Where, however, they lie within the second zone near its outer limit, this bounding line is bowed outward.

Fourth Zone. This zone, which reaches 1.25 mm. in width, consists of clouded potash-rich feldspar having distinct radial growth, and widely scattered acmite. The inner edge of the zone is not well-defined, but its outer edge is clearly marked by a deeply lobed contact against the much more densely clouded plagioclase-rich interspherulitic areas. The acmite granules reach diameters of 10 μ. The zone is characterized by numerous, small, radially-elongate areas up to 0.2 mm. long composed of clear quartz and plagioclase. These areas, like the crescents of the third zone, are bounded by dark cloudy rims, but none is large enough to possess distinct lateral or terminal concentrations of acmite. It is probable that they have the same origin as the crescentic areas and that their shapes have been determined by the radial growth of isolated quartz crystals.

A few oval to nearly circular clear areas, up to 0.8 mm. in diameter, consist of relatively coarse equigranular quartz. These areas are rimmed by dark borders of dense cloudy material and some acmite, and differ only in size, shape, and lack of fibrous habit from the structures described above.

Interspherulitic Areas. These cuspate areas range in width from about 2 mm. where the spherulites are widely spaced, to thin lines where they are closely packed. These areas are composed chiefly of densely clouded feldspathic material lacking distinct radial growth, and of small central areas rich in granular quartz. Stain tests show that the clouded matrix is made up almost entirely of plagioclase, but that potash feldspar is locally present in the vicinity of the quartz. The central cuspate areas consist of quartz in interlocking grains up to 0.1 mm. in diameter together with small fibers of plagioclase and, in a few places, large radiating fibers of acmite. Densely clouded rims are characteristic of these quartz-rich patches. More or less circular clear areas, similar to those occurring in the fourth zone, may also be present.

General Observations. Several observations regarding the character and distribution of the minerals of the feldspathic spherulites follow. The paragenesis is shown diagrammatically in Fig. 4.

1. Acmite, which is most abundant in the first zone, decreases abruptly in concentration at the contact with the second zone, and is present in only minor amounts in the outer zones except at the margins of the quartz areas. Locally, however, it is abundant in masses of quartz in interspherulitic areas. The average size of the acmite granules increases between the center and the margin of the first zone and then declines gradually in outer zones. The radiating fibers of acmite of the interspherulitic areas are different in habit from the granules in the spherulites.

2. Riebeckite (?) is present in an amount apparently inversely proportional to that of acmite. It is absent in the central part of the first zone where acmite is abundant, and present in considerable amounts in the second zone where acmite is scarce. Change in riebeckite content from the second to the outermost zone is not determinable. Two generations can be recognized: relatively large prisms in the outer part of the first zone, and minute to submicroscopic needles in the other zones. Al-

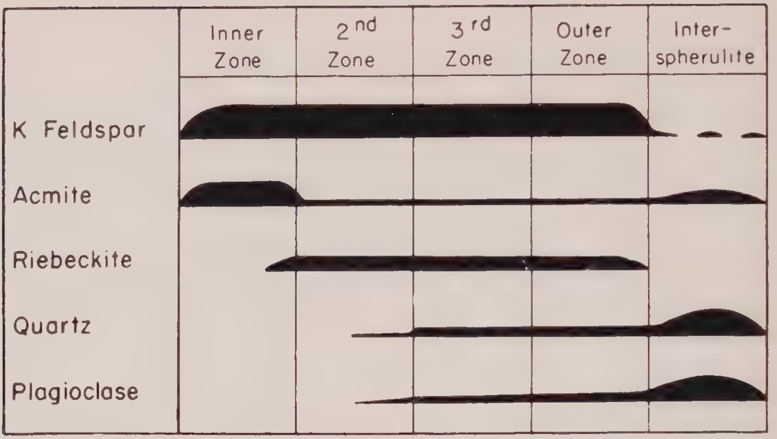

FIG. 4. Diagram showing paragenesis of minerals in central part of Nazcha Valley dike.

though the decline in grain size from the first to second zone is abrupt, the decline in size of the needles from the inner edge of the second zone to the outermost zone is gradual.

3. The potash feldspar of the first zone forms irregular interlocking grains, whereas that of the outer zones forms radial fibers. Although potash feldspar makes up the greater part of the spherulites, it is absent from interspherulitic areas except in halos around patches of quartz.

4. Quartz is found almost exclusively in the interspherulitic areas and in clear areas of crescentic, radially elongate, and oval to circular shapes in the third and fourth zones of the spherulites. It tends to form relatively coarse crystals of either fibrous or equigranular interlocking habit.

5. Plagioclase, which generally is fibrous, is found almost exclusively in the interspherulitic areas and in or adjacent to the clear quartz-rich areas in the outer zones of the spherulites.

Flow Layers of the Nazcha Valley Dike

The flow layers of the Nazcha Valley dike (locality A, Fig. 2) are made up of cloudy, finely-crystalline layers alternating with more coarsely-crystalline layers of quartz and conspicuous riebeckite needles (Fig. 3-1). The cloudy layers, 0.035 to 0.8 mm. in width, are composed of minute needles of riebeckite up to 10 μ in length in a colorless weakly birefringent matrix with an index close to that of balsam. Stain tests show this to be mainly potash feldspar. The clear intervening layers, 0.04 to 1.40 mm. in width, are composed of quartz and needles of riebeckite, or of acmite (?) pseudomorphous after riebeckite, forming narrowly radiating bundles extending from both walls toward the center of the layers. Most of these needles are straight, but in a few of the wider layers they apparently tended to bow slightly to one side during their growth and they meet in a central zone in which needles of acmite (?) and minor riebeckite are arranged parallel to the layers. A few spherulites composed of radiating fibers of acmite (?) and riebeckite in a quartz-rich matrix may be present in the central parts of some of the wider layers, and hemispherical aggregates of similar composition are present locally along their walls. Neither the quartz nor the delicate needles of riebeckite in the clear layers shows any strain even at points where the flow layers are markedly contorted; hence it seems that these minerals crystallized after injection of the dike had been completed.

Spherulitic Dikes of Glundebery Valley

The spherulites of the Glundebery Valley dikes (locality B, Fig. 2) range from 0.4 to 3.5 mm. in diameter. They consist of radiating needles of riebeckite, or its alteration product composed of black opaque grains, goethite, and hematite, in a matrix of fine radiating fibers of feldspar which is mainly potash-rich. Many of the larger spherulites have grown around quartz or microperthite phenocrysts, but most of the smaller more closely packed spherulites lack such nuclei. Where phenocrysts have served as centers of crystallization, needles of riebeckite and fibers of feldspar tend to radiate from some of the corners or edges of the phenocrysts rather than from their faces (Fig. 3-5). The outer rim of a typical spherulite consists of micrographic quartz and potash feldspar together with ends of the radially-arranged riebeckite needles and additional stouter prisms of riebeckite similar to those of the interspherulitic areas (Fig. 3-6). These stouter riebeckite prisms show a preferred orientation parallel to the rim of the spherulite and may have been rotated into this position prior to engulfment in the growing spherulite.

Another dike in this locality contains indistinct spherulites composed mainly of intergrowths of quartz and radiating feathery feldspar. These irregular coalescent spherulites rarely exceed 6 mm. in diameter. Mixtures of black opaque grains and hematite pseudomorphous after riebeckite needles tend to have a rough radial arrangement in some places and in one place, a tangenital arrangement, but in most parts they are oriented at random. The radiating clusters of pseudomorphs after riebeckite needles commonly transgress fibers of the quartz and feldspar intergrowths. Although in the highly spherulitic rhyolite from this locality both the riebeckite and feldspar fibers radiate from a common center, this rule does not necessarily apply to the imperfectly spherulitic dike.

The interspherulitic parts of the dikes of Glundebery Valley described above and the non-spherulitic rhyolite at this locality are made up of

TABLE 1

	1	2	3	4
CHEMICAL ANALYSES*				
SiO_2	74.42	77.29	75.83	72.80
TiO_2	0.21	0.15	0.26	0.33
Al_2O_3	8.58	9.27	10.35	13.49
Fe_2O_3	3.44	2.07	4.35	1.45
FeO	3.07	1.36	0.54	0.88
MnO	0.11	0.04	0.05	0.08
MgO	0.34	0.09	0.26	0.38
CaO	trace	0.34	0.18	1.20
Na_2O	4.33	4.01	2.66	3.38
K_2O	4.75	4.54	4.59	4.46
H_2O+	0.29	0.37	0.92	1.47
H_2O-	0.10	0.08	0.07	—
P_2O_5	n.d.	n.d.	n.d.	0.08
ZrO_2	0.46	0.41	0.14	n.d.
Total	100.10	100.02	100.20	100.00
NORMS				
Apatite	—	—	—	0.20
Ilmenite	0.40	0.29	0.49	0.61
Zircon	0.68	0.61	0.21	—
Orthoclase	28.15	26.90	27.20	26.69
Albite	17.63	22.36	22.57	28.45
Anorthite	—	—	0.89	5.28
Corundum	—	—	0.66	1.12
Acmite	9.97	6.00	—	—
Sodium metasilicate	1.81	1.13	—	—
Magnetite	—	—	1.16	2.09
Hematite	—	—	3.55	—
Diopside	—	1.46	—	—
Hypersthene	6.36	1.78	0.65	0.95
Quartz	34.71	39.03	41.83	33.18
Water	0.39	0.45	0.99	1.47
Total	100.10	100.01	100.20	100.04

* 1, 2, and 3 analyzed by Chief Analyst and Assayer, British Columbia Department of Mines.

1. Zone of contorted flow layers, Nazcha Valley.
2. Spherulitic zone, Glundebery Valley.
3. Non-spherulitic zone, Glundebery Valley.
4. Average rhyolite, including 24 liparites (Daly, 1933, p. 9).

equigranular interlocking quartz and feldspar. The riebeckite in the interspherulitic areas differs from that in the spherulites by having a distinctly stouter habit and by being much more highly altered to trains of black opaque minerals and hematite. In the non-spherulitic rhyolite, no riebeckite is present and not even psuedomorphs were seen. Instead, more or less equant interstitial grains of black opaque minerals and goethite are scattered throughout the rock in abundance.

Chemical Composition

Analyses of three samples of the rhyolites are given in Table 1 and an average composition of rhyolite (including liparite) computed by Daly (1933, p. 9) is included for comparison. The rhyolites from the Atsutla Range are clearly deficient in alumina and lime, but abnormally rich in ferric iron, and to a lesser extent, in ferrous iron.

Each of the three analyzed rhyolites contains modal albite, potash feldspar, and quartz, which are abundant in their norms (Table 1). In samples 1 and 2, riebeckite, acmite, and decomposition products of riebeckite can account for most of the excess soda and iron indicated by the normative acmite, sodium metasilicate, diopside, and hypersthene.

Conclusions

Crystallization of the groundmass of the rhyolite dikes occurred after the dike-magma came to rest; otherwise, the delicate fibers of the spherulites and axiolites would show damage from contact with one another. To preexisting inhomogeneity in the magma of the Nazcha Valley dike can be ascribed the layering in its marginal zones; this layering was contorted by viscous drag against the dike walls during emplacement of the melt. The Glundebery Valley dikes seem to have been homogeneous at the time of intrusion except for scattered phenocrysts.

Pressure did not necessarily remain uniform once the magma had reached its final position, nor did temperature necessarily decline continuously. Minor changes in gas content, vapor pressure, and confining pressure could take place with time. Heat supplied by crystallization might locally and temporarily balance loss of heat to the walls of the dike and if appreciable supersaturation of some constituents existed, some excess heat might be evolved on rapid crystallization which could bring about a local rise in temperature. Such changes in conditions during cooling might account for the reversal in the sequence of crystallization of acmite and riebeckite and for the sharp breaks in conditions of crystallization in the spherulites of the Nazcha Valley dike.

A close relationship between riebeckite and acmite is shown in the rhyolites described above and in many other rocks bearing these minerals.

The stability ranges of these two minerals are, however, not well known. The transformation of riebeckite to acmite can be expressed by the equation:

$$\underset{\text{Riebeckite}}{(OH)_2Na_2Fe_3''Fe_2'''(Si_4O_{11})_2} = \underset{\text{Acmite}}{2NaFe'''Si_2O_6} + \underset{\text{Ferrosilite}}{3Fe''SiO_3} + SiO_2 + H_2O$$

Assuming densities of 3.40, 3.60, 3.95, 2.65 for riebeckite, acmite, ferrosilite, and quartz respectively, we find that the molecular volume of riebeckite (275) slightly exceeds the total of those of its solid decomposition products (251). The molecular volume of water vapor, itself a function of both temperature and pressure, is, therefore, critical in determining the effect of pressure on this transformation. It is apparent from data on the specific volume of water vapor (Birch, 1942, p. 211) that at depths of less than some tens of kilometers and temperatures of some hundreds of degrees or more, increasing pressure favors the development of riebeckite and vice versa. Such a conclusion is in accord with that deduced from petrographic studies of hornblende and pyroxene in volcanic rocks in which hornblende is considered to be a deep-seated mineral, and pyroxene one capable of crystallizing at shallower depths. The effect of temperature on the riebeckite–acmite transformation is not known.

The relationship between riebeckite and acmite and the black opaque minerals, goethite, and hematite is also close, although again little is known of the stability ranges of the minerals. Experimental work shows that acmite melts incongruently at 990° C. to form hematite and a liquid richer than acmite in silica and soda (Bowen & Schairer, 1929). It has been found that hornblende and pyroxene of lavas become unstable under conditions of diminished pressure and slow cooling from a relatively high temperature and tend to break down into pseudomorphs of iron ores (MacGregor, 1938, p. 54, p. 56). In lavas, the reduction of pressure is caused by extrusion and temperature is maintained, or even increased at the surface, until the change takes place. It is difficult to see how pressure could be markedly reduced during crystallization in the dikes of the Atsutla Range before they became cold.

The origin of the clear crescentic areas of quartz and minor feldspar in the sections of the third zone of the Nazcha Valley dike presents an interesting problem. At first glance, they might be regarded as the fillings of open concentric cavities like those of lithophysae. Such, however, does not seem to be the case. Quartz crystals have not grown from opposite walls to meet in an irregular sutured boundary midway between them; instead, most of the individual crystals extend from wall to wall. The concentration of acmite at the outer side of the crescents can best be explained by the mechanical displacement of acmite crystals, previously disseminated through the cooling magma, by the force of growing crystals of quartz which began their growth on what is now the inner margin of the crescents and became extended normal to these surfaces. This mechanism accounts for the similarity in size, shape, and optic characters of the acmite grains at the edges of the crescents to other grains of that mineral scattered through the adjoining parts of the spherulites. The fact that the ratio of the width of the acmite rim to the width of the entire crescent conforms closely to the ratio of acmite to matrix in neighboring areas is likewise in accord with the postulated mechanism. The cloudy concentrations of riebeckite (?) immediately outside the crescents may be accounted for in the same way although the grains of this mineral are too fine to show similarity in shape and optic characters to those farther from the crescents. The mechanism presumes that within the third zone quartz developed on the surfaces of the growing spherulites which had hitherto been composed principally of potash feldspar. The potash feldspar, apparently incapable of forcing aside the granules of acmite and needles of riebeckite, had engulfed these impurities; needles of quartz, on the other hand, apparently were able to push the solid particles ahead of their growing tips. The work of Becker & Day (1905, 1916), Correns (1926), and others, (see Buckley, 1951, pp. 468–479) has shown not only that forces of repulsion between a growing crystal immersed in a supersaturated liquid and an adjoining solid can exist, but that the forces can vary with the surface characters of the two solids in contact with one another. Growth of individual quartz masses on the spherulites may have become effectively retarded when their outer surfaces had become thoroughly encrusted with granules of acmite and mats of riebeckite. Up to this stage, however, growth of quartz may have exceeded that of feldspar, for in one place where quartz has developed immediately inside the cloudy growth line marking the outer limit of the second zone, this line shows a distinct bulge.

The zirconia content of the dikes attains unusually high though by no means unprecedented values. The average content of zirconia in 80 German occurrences of "granite" is about 0.034% according to v. Hevesy & Würstlin (1934, p. 308), less than one tenth that of the two analyzed spherulitic dikes of the Atsutla Range. According to these authors (1934, p. 309), "soda granites and soda syenites" have an average content of 0.067% zirconia (26 occurrences from various sources) and "potash granites and potash syenites" have an average of 0.084% zirconia (24 occurrences from various sources). Appreciably higher amounts of zirconia, however, have been reported elsewhere. A sample of rockallite analyzed by Washington (1914, p. 297) contains 1.17% zirconia and samples of granite from the Ampasibitika area of Madagascar contained from 0.50 to 3.71% zirconia according to Lacroix (1903, p. 235).

It is of interest that these zirconia-rich rocks from British Columbia, Rockall, and Madagascar are rich in riebeckite and aegirine, acmite, or arfvedsonite. The zirconia content of the Madagascar granites was attributed by Lacroix (1903, p. 236) to the presence of abundant zircon. Since zircon is rare in the sample from Rockall, however, Washington concluded that the zirconia is present in the acmite and calculated that it contains 2.67% zirconia (1914, p. 300). He suggested that the distinction between the yellow-brown pyroxene referred to as acmite and the greenish kind called aegirine may be connected with the presence of zirconia or oxides of rare earths in the former and their absence from the latter (1914, p. 301; 1927, p. 233, 248). In the spherulitic rhyolite dikes of the Atsutla Range, zircon occurs only with intensely altered riebeckite but not with this mineral in its unaltered state, and the pyroxene is a pale yellow variety. For these reasons, it is suggested that the riebeckite and acmite of the rhyolites may contain appreciable amounts of zirconia in solid solution.

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DECREPITATION CHARACTERISTICS OF SOME HIGH GRADE METAMORPHIC ROCKS

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Abstract

The decrepitation characteristics of several types of high grade metamorphic rocks from 17 localities were determined. A similar stage of decrepitation was found in every specimen, starting at temperatures from 565 to 710° C., the average value being 633° C. The cause of this stage of decrepitation tentatively is interpreted to be due to the misfit of crystalline inclusions in the constituent minerals when they are heated above the temperature at which they crystallized.

Introduction

The decrepitation characteristics of a number of varieties of garnet were reported recently (Smith, 1952b). Several stages of decrepitation were recognized, and one, ascribed to differential thermal expansion of crystalline inclusions, was found to begin at some temperature between 300 and 700° C. This stage of decrepitation (here designated as the D2 stage) was found to be a function of the abundance of crystalline inclusions in the garnet. Grossularite and andradite were found to have a much lower D2 temperature than almandite and pyrope. Garnets of different composition from the one locality were found to have the same D2 temperature, and hornblende closely associated with almandite was found to have a D2 temperature very similar to that of the garnet.

The above data suggest the possibility that metamorphic minerals, which usually contain a great abundance of crystalline inclusions, may be found to have decrepitation characteristics which reflect the conditions during growth. Stated in another way, if decrepitation of metamorphic minerals beings at a temperature below that of formation, and continues above it, some change would be expected in the rate of decrepitation when the minerals are heated above the maximum temperature which they had already experienced. If a mineral be heated to some temperature, t, in the laboratory, then cooled, crushed, and heated again, a sudden increase in rate of decrepitation takes place at the temperature t. This fractional increase in rate of decrepitation at t is greater when the fractional degree of comminution after preheating is smaller. When the specimen is crushed before preheating and not afterward, there is practically no decrepitation until the temperature t is reached, and there is a very rapid increase immediately above t. Similarly, if a mineral encloses other minerals as it grows at temperature t, decrepitation should be greater above this temperature than below it (Smith, 1952a), and if all the minerals in one rock crystallized (or recrystallized) at the same temperature, they should have similar temperatures of D2 decrepitation. Taking this as a working hypothesis, it is unnecessary to separate single minerals of metamorphic rocks for decrepitation analysis, and the rock as a whole may be studied.

The interpretation of complex decrepigraphs is not simple and the criteria of cause of each stage have not been determined exactly. At the present time in this laboratory, the following criteria are being employed in the case of metamorphic minerals.

1) Decrepitation starting below 350°, usually between 200 and 300°, and not very vigorous, is due to filling of complex inclusions by the liquid phase. This is somewhat analogous to decrepitation of hydrothermal minerals due to filling of simple two-phase fluid inclusions by the liquid phase, and is virtually absent in garnet of regionally metamorphosed rocks. The symbol being used for this type of decrepitation is D1.

2) Decrepitation which starts fairly sharply at 300–700° C., rises within about 100° to its maximum rate, and continues for several hundred degrees, may be due to solid inclusions if no other facts conflict with this interpretation. Decrepitation beginning above 450° C. cannot be D1, if the solutions are aqueous. Below this temperature, ambiguity may be removed by use of a heated microscope stage. The symbol being used for decrepitation due to solid inclusions is D2.

3) Decrepitation which starts indefinitely, and continues to accelerate until nearly the peak rate is reached at 360–450° C. is characteristic of the soft hydrothermal minerals, and especially the carbonates. The cause has not been determined, but the facts that a) the curve of rate *vs* temperature resembles the curve of pressure *vs* temperature for water solutions, and b) the peak rate is near the critical temperature of water and salt solutions, both suggest that water in imperfections of the minerals may be responsible. The symbol being used for this type of decrepitation is D3.

4) Decrepitation due to inversion should begin and reach its peak rate within a few degrees, but in the case of quartz, there appears to be a preliminary decrepitation which is evident at least 70° before the inversion, continues to accelerate to a sharp peak rate at the α-β inversion ($573 \pm 3°$ C.), and then falls very rapidly. The symbol being used for decrepitation due to inversion is D4.

5) Decrepitation due to decomposition, such as dehydration of gypsum and goethite, usually is too faint to detect, unless the water condenses and boils on the walls of the heating device. Exfoliation of micaceous minerals, such as chlorite, usually can be detected by the apparatus now in use. This gives a rapid increase in rate, with a well-defined peak and rapid decrease in rate. When decomposition is suspected, the responsible

mineral can be determined by running the component minerals of the rock and comparing the peak rates. The symbol being used for decrepitation due to decomposition is D5.

6) The decrepitometric and microscopic data on metamorphic minerals recently obtained in this laboratory suggest that if liquids are present during growth, they are siliceous rather than aqueous, although water may be present as a component; the temperatures of formation are approximately 300–700° C.; contact metasomatism of limestone with formation of silicates takes place at approximately 300–500° C.; formation of garnetiferous granite gneiss takes place at approximately 600–700° C.

When a new technique is developed to study an old problem, there arises a choice of methods of use of the new data. One may set out to test each of the older hypotheses and theories by a suitable set of critcial experiments, or one may build a new set of internally consistent hypotheses to satisfy the new data. In the field of physical chemistry of metamorphic processes, for a long time dominated by abstruse and cyclic logic, the second course is indicated. The critical reader will have noted the mass of unwarranted speculations which have become interlocked and taught as fact. Temperatures of metamorphic grades are given, without a measurement having been made. Shearing stress is stated to be a phase determinant, without facts. Water solutions as interstitial catalysts are postulated, but the distinctive metamorphic minerals such as cordierite, almandite, staurolite, kyanite, etc., have not been synthesized in water solutions. Accordingly, generalizations made on the basis of the following decrepitation results will not be within the framework of any current theory of metamorphism.

The rocks selected for this series of tests contain minerals which have been found in preliminary studies to give fairly vigorous decrepitation. Very fine grained minerals, and soft minerals, generally give too faint or infrequent decrepitation for good rate analysis and recording by the present equipment. Therefore, the metamorphic rocks which give easily resolvable decrepitation are those of high grade regional and contact metasomatic type. While these types cover only a limited range of metamorphic conditions, they would serve to establish some limits of temperature during metamorphism, if the temperature during crystallization is reflected in their decrepitation.

Decrepitation Data

The decrepitation method has been described several times in the past by Scott (1948), Peach (1949), and Smith (1952a). A more complete description of the electronic system and heating apparatus is being prepared for publication.

The present standard method of treatment includes the following steps: a) crushing and sieving to −40+80 mesh, b) digestion in hot hydrochloric acid to remove carbonates if present, c) heating 1–3 cc of the preparation in the decrepitation apparatus at 10–20°C per minute, d) electronic analysis of the rate of decrepitation, recorded as a curve of rate *vs* time, with or without supplementary cumulative summation of the number of detected explosions, e) automatic temperature fiducial marks made on the rate/time curve at 20° intervals, and f) corrections applied to the interpolated temperature of discontinuities on the rate/time curves by a calibration chart prepared in October, 1950.

The probable error of reading a discontinuity on electronic decrepigraphs is about ±5°, and the accuracy of any one reading is about ±10°, determined by the scatter of values during the original calibration tests. Unless the discontinuities on the curves are very sharp, wider limits of accuracy, ±20°, are given below.

The following decrepitation data are grouped in several ways to answer a number of obvious questions which would arise as to the probable meaning of the results.

Different minerals in the same rock

Barton Mine, New York. Red garnet and green hornblende from the Barton Mine, New York, were previously reported to have a high temperature decrepitation beginning at 613±30 and 603±20° C., respectively (Smith, 1952b).

Willsboro, New York. An intergrowth of andradite garnet and white wollastonite from Willsboro, New York, obtained from Ward's, was separated into pure components after coarse crushing. The garnet was reported to have compound decrepitation, one curve starting between 300 and 400°, and another starting at 594±10° (Smith 1952b).

The Wollastonite decrepitated very vigorously starting at 275±20°, with a peak rate near 375°, and on the downward slope, an increase began at 581±20°. Considering the uncertainty of interpreting the complex curves, the high temperature decrepitation of both the garnet and wollastonite probably starts at the same temperature (590±20°, weighting in favor of the garnet results).

Different rock compositions in the same locality

O'Connor Lake, N.W.T., Canada. Two highly metamorphosed rocks from a band of schist and gneiss at O'Connor Lake. N.W.T. (Lat. 61°15′N, Long. 111°50′W) were available for testing. One specimen is a course grained garnetiferous gneiss, containing abundant pink feldspar, a little dark mica and pink garnet, and not much quartz. This began to decrepitate feebly at about 255°, increased somewhat after 330°, and reached a peak rate near 430°. The quartz inversion curve was evident but not high. A vigorous stage of decrepitation began at 635±20°, reached a peak rate near 700° and then fell rather rapidly. The other specimen is a coarse grained hornblende gneiss, containing dark green hornblende and clear, colorless, plagioclase. This began to decrepitate at 370±10°, and rose to a peak rate near 540°. Another increase began at 632±20°, with a peak rate near 730°. The temperature of beginning of the last stage of decrepitation of the two rocks is measurably the same (633±20°).

Similar rocks from different localities. a) Amphibolite

Barton Mine, New York. The decrepitation temperatures of garnet and hornblende from the Barton Mine, New York, may be taken to represent that of the rock in which they occur, since they are the principal minerals. The mean D2 temperature, weighted in favor of the value for the more abundant hornblende, is 606±30°.

Bryce Township, Ontario. A specimen of amphibolite from a small xenolith in granite was obtained from a suite collected by W. W. Moorhouse. The occurrence is in a granitic intrusion breccia, 50 feet from the contact with metamorphosed basalt, in Range 6, Lot 12, Bryce Township, 25 miles south of Kirkland Lake, Ontario (Map 50j—*Ontario Department of Mines*).

Very little decrepitation was detected below 500°. A rate curve began feebly at 525±30°, and increased at 640±20°, with a peak rate at 720±20°.

Cadillac Twp., Quebec. Two specimens of amphibolite schist from the O'Brien Gold Mine, Kewagama, Quebec, were obtained from a suite collected by R. Blais. Specimen A contains actinolitic hornblende, brown tourmaline, and some biotite. Apparently it has been derived from the regional greenstone by metasomatism. Specimen B contains less tourmaline, more biotite, and some chlorite. It occurs in close association with lenses of dark colored albite porphyry. Both specimens were treated with warm hydrochloric acid after grinding, to remove a small amount of a carbonate mineral.

Specimen A gave a complex decrepigraph. The first evident rate curve began at 342±20° and reached a peak rate near 440°. Another increase began sharply at 581±20° and this curve continued to increase in rate to 750°, the limit of heating.

Specimen B gave a somewhat similar complex decrepigraph, but the rate was only about one fifth of that of Specimen A. The first curve began at 425±40°, and the second, at 620±20°.

Calumet Island, Quebec. A specimen of amphibolite was obtained from a suite collected by W. W. Moorhouse from the property of New Calumet Mines, Ltd. This locality contains a complex group of rocks which have been interpreted to be due to metasomatic alteration of sediments by pegmatitic solutions (Moorhouse, 1941).

Decrepitation was very feeble until 652 ± 20°, when a well-defined stage began fairly abruptly. The peak rate was above 750°, the limit of heating. The decrepigraph, corrected for heating rate lag, is shown in Figure 1.

Hybla, Ontario. A specimen of massive black amphibolite interbedded with crystalline limestone near Hybla, Ontario, was obtained from a suite collected by P. A. Peach, who interprets the occurrences as amphilolite developed in limestone due to pegmatitic metasomatism. The locality , 10 miles due north of Brancroft, is well known for a number of large bodies of granite pegmatitite (Ellsworth, 1932).

The decrepitation of this specimen (cleaned with hot hydrochloric acid to remove a small amount of carbonate), started at 335 ± 20°, reached a peak rate near 420°, and began to increase again at 475 ± 20°. This curve reached a flat maximum rate near 540°, began to increase again at 612 ± 10°, and reached a peak rate near 720°. Some of the same preparation was treated with warm dilute hydrofluoric acid to remove most of the quartz and feldspar. The decrepigraph showed a decrease in the maximum rates, the curve starting at 335° was missing, the curve starting at 475° was of low intensity, and the highest temperature stage started at 625 ± 10°, which probably is higher than the first value obtained.

Lake Athabaska, N.W.T. Two specimens of schistose amphibolite from the north shore of Lake Athabaska (Lat. 59°35′N, Long 108°40′W) were obtained from a suite collected by H. G. Harper. Both specimens are from different bands of amphibolite within garnetiferous granite, both of which may be metamorphosed sediments. Specimen A was from an underground working, and specimen B, from the surface, about 125 feet from specimen A.

Specimen A began to decrepitate vigorously starting at 370 ± 20°, and reached a peak rate near 450°. An even more vigorous stage began less definitely at 595 ± 20°, with a peak rate near 750°, the limit of heating.

Specimen B decrepitated less vigorously, starting at 360 ± 20°. The rate reached a minor peak near 510°, then soon started up on a quartz inversion curve with a peak at 575 ± 10°. On the fall in rate, an increase began at 595 ± 20°., and the peak rate appeared to be near 750°, the limit of heating.

Long Lake, Olden Twp., Ontario. A specimen of gneissic amphibolite

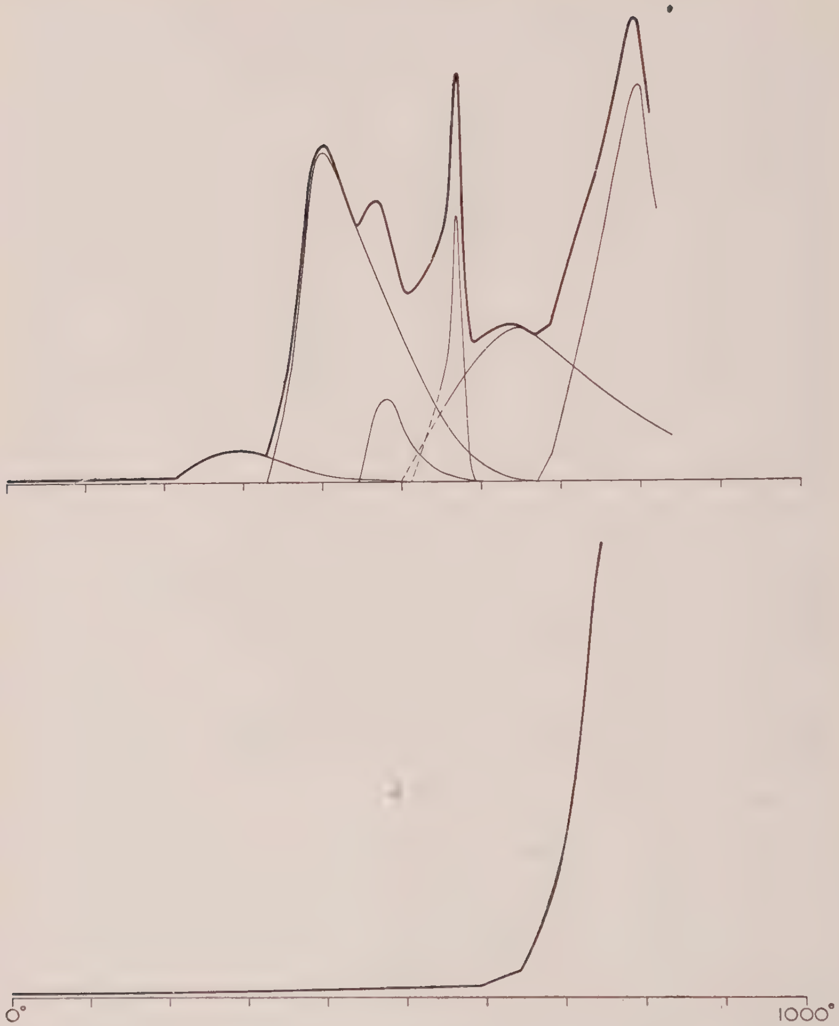

FIG. 1. (Top) Complex decrepigraph of granite gneiss from Bobcaygeon, Ontario, showing six stages of decrepitation and deduced simple rate curves. (Bottom) Simple decrepigraph of amphibolite from Calumet Island, Quebec.

was obtained from a suite collected by P. A. Peach. The locality is on the north side of Long Lake, Olden Township, Ontario, about one half mile west of the east end of the lake, and near a large batholith of granite and/or syenite. The specimen was taken one inch away from a dike of aplite, 10 inches wide, of which there are a number intruding the amphibolite. The geology of the area, which lies north of Kingston, was described by Harding (1947).

Decrepitation began sharply at 133±10° and reached a peak rate near 240°. An increase began at 333±20, and appeared to consist of several unresolved curves until 650±20°, when a well-defined rate increase began. The peak rate was near 730°.

Yellowknife, N.W.T. Several specimens of greenish black amphibolite from Yellowknife, N.W.T., were obtained from a suite collected by R. W. Boyle. The location is north and west of the town, between the large granite batholith to the west of, and the sedimentary series to the east of, a belt of metamorphosed basalt and other extrusives. The geology of the area is shown in Maps 709A and 868A, Geological Survey of Canada.

A stage of decrepitation began at 355–410°, reached a peak rate between 400 and 500°, but sometimes increased again between 500 and 600°, probably due to quartz. A vigorous stage began at 610°–665°, with a peak rate above 720° in all cases. Variations within these limits are described below.

Wilberforce, Ontario. A coarse grained amphibolite from Wilberforce, Ontario, was obtained from a suite collected by W. W. Moorhouse. The specimen occurs one inch away from a pink pegmatite which contains large hornblende crystals with fluorite and calcite. The occurrence was described by Ellsworth (1932, pp. 213–227).

The decrepitation was found to be complex. The first rate curve began at 332±10° and reached a peak rate near 400°. A small rate increase typical of quartz inversion obscured the start of a vigorous stage, but it appeared to begin at 575±20°. The peak rate of this curve was at 700±20°.

Similar rocks from different localities. b) Paragneiss

Bobcaygeon, Ontario. A specimen of coarse grained granite gneiss, probably a metamorphosed sediment, was obtained from a glaciated outcrop 30 miles south-west of Bobcaygeon, Ontario (Lat. 44°25′N, Long. 78°35′W). Under the microscope, the rock was seen to be composed of clear colorless microcline, nearly clear plagioclase, quartz, and a small amount of biotite. After crushing, the specimen was acid washed to remove a slight rusty stain, and all but traces of the biotite were removed by jigging and panning.

The decrepitation was vigorous and complex. The first stage began at 216±20°. The second stage, apparently composite, began abruptly at 320±20°, and reached a peak near 460°. A quartz inversion rate curve rose on the descent of the second rate curve. Another stage began sharply at 610±20° and another began at 690±20°. The last stage of decrepitation was vigorous, with a peak rate above 750°, the limit of heating.

In order to determine the effect of the mica alone, a concentrate containing mostly mica was prepared. This gave feeble decrepitation. All of the stages described above appeared, except the one at 690 ± 20°. Considering the relative peak rates of the various stages in the two runs, it was deduced that the small amount of mica impurity in the sample was not responsible for any of the recorded stages of decrepitation.

Several runs were made, varying instrumental settings of gain and integration characteristics, and grain size and mineralogy of the specimen, in order to obtain maximum resolution of the complex series of rate curves starting between 500 and 700°. It was found that the D3 curve is much less evident using a finer grain size, such as $-80+200$, and, since the high temperature curves are easier to deduce and subtract from the composite when the base line is flatter, this grain size was used in most of the tests. In the decrepigraphs, the quartz inversion curve is considerably greater than the one immediately following, which makes resolution uncertain. Accordingly, some of the quartz was removed by heavy liquid separation from the slightly lighter feldspar. The remainder, free from mica and any other heavier minerals, if present, and containing only a small amount of quartz, gave the best rate curves for analysis.

The complex decrepigraph is shown in Figure 1. This is derived from one run, but qualitatively is representative of all of them. The curves are corrected for heating rate lag. Six component curves are show in the figure, but these are only tentative solutions.

Barry Bay, Ontario. A specimen of coarse grained banded grey paragneiss was obtained from a road cut one mile south of Barry Bay, Ontario (Lat. 45°30′N, Long. 77°40′W). In hand specimen, the rock is composed of nearly equal amounts of white feldspar and black hornblende, with a small amount of black biotite and quartz. After crushing, the specimen was digested in hot hydrochloric acid, and most of the biotite was removed by jigging and panning.

The decrepitation was fairly vigorous, and also complex. The first stage began at 340 ± 20° and reached a peak near 410°. Another stage began between 400 and 500°. A very small quartz inversion curve was evident. The high temperature stage began abruptly at 700° ± 20°, and rose to a peak rate at about 820°.

Bracebridge, Ontario. A specimen of grey paragneiss, very similar to the above specimen from Barry Bay, was obtained from a road cut near Bracebridge, Ontario (Lat. 45°0′N, Long 79°20′W). In hand specimen it appeared to contain a little more feldspar than the former. It was cleaned and washed in a similar manner.

The decrepitation was vigorous and complex. The first feeble stage began between 200 and 300°. The first vigorous stage began at 340 ± 20° and rose to a peak rate near 430°. Possibly another stage began between 400 and 500°. A good quartz inversion curve appeared. The high temperature stage began at 705 ± 20° and rose to a peak rate near 810°.

Whitney, Ontario. A specimen of coarse grained, banded, grey, granitic gneiss was obtained from a road cut six miles east of Whitney, Ontario (Lat. 45°30′N, Long. 78°05′W). This rock varies in texture and composition and would be classed as a paragneiss, or migmatite, or gneissic intrusive by competing theorists of origin of granitic rocks. The ferromagnesian minerals are black biotite and hornblende, and quartz is present. The ratio of dark to light minerals is about that of granodiorite.

Decrepitation was fairly vigorous and very complex. The first stage started at 350 ± 20° and reached a peak rate near 440°. Another stage, possibly compound, began near 490°. The quartz inversion curve was very evident. The high temperature stage began at 710 ± 20° and reached a peak rate near 820°.

Similar rocks from different localities. c) Chlorite Schist

Soft minerals have been found to give very little detectable decrepitation, except at decomposition temperatures in some cases. Therefore chlorite schist is not suitable for decrepitation studies, unless it contains brittle metacrysts, which may be removed and treated separately.

Snow Lake, Manitoba. A specimen of garnetiferous chlorite schist from the 580 Level, Snow Lake Mine, Snow Lake, Manitoba (Lat. 54°50′N, Long. 100°00′W) was made available by F. Ebbutt. The garnet metacrysts are pale red in color, with abundant crystalline inclusions. They have mirror-smooth faces against the schist matrix, which consists of chlorite and a small amount of amphibole and white minerals. The rock is metamorphosed dike, and, from the abundance of dark minerals, probably was originally a diabase.

A preparation of the pure garnet gave a very little low temperature decrepitation. A small quartz inversion rate curve was recorded, near the peak of which a fairly vigorous stage began, at 580 ± 20°. There appeared to be another increase at 678 ± 20°, with a peak rate near 740°.

A preparation of the matrix, not chemically treated, gave very little decrepitation until a rate curve began at 563 ± 10°. This seemed to be composite, and at 691 ± 20° a very vigorous stage began.

Probably the highest temperature stage of decrepitation is due to decomposition of chlorite. The stage beginning at 580° (garnet) and 563° (matrix) may be the D_2 stage. A weighted mean value for the rock is 565 ± 20°.

Similar rocks at different distances from intrusives

Renfrew, Ontario. Several specimens of impure crystalline limestone, near a large body of granite, were available in a suite collected by the writer several years ago. The locality is 4 miles south of the town of Renfrew, Ranges III and IV, Lot 1, Admaston Township. The geology of the area is shown on Map 53b, Ontario Department of Mines. The first tests gave no useful decrepitation results, due to the extremely vigorous effect of the carbonates, starting near 300°, which masks decrepitation of the various silicate minerals present. Therefore all carbonate minerals were removed with boiling concentrated hydrochloric acid before heating in the decrepitation apparatus.

Specimen A (F.G.S. No. 2) began to decrepitate at 210 ± 30°, reached a minor peak rate at 320 ± 30°, began to increase again at 340 ± 30°, reached another peak rate at 495 ± 20°, increased again to the quartz inversion temperature, and then began a vigorous stage which, when projected back, appeared to start between 525 and 620°. The sharpest positive change of rate was at 615 ± 10°.

Specimen B (F.G.S. No. 9) began to decrepitate indefinitely about 355 ± 30°, and the rate curve was obviously composite, with a peak rate at 590 ± 20. A more vigorous stage began at 608 ± 20°, reaching a peak rate at 695 ± 10°.

Specimen C (F.G.S. No. 35) began to decrepitate feebly about 275 ± 30°. Another stage began at 365 ± 30°, with a peak rate near 480°. A slight increase typical of quartz was evident, but a definite increase began at 585 ± 20°, with a peak rate at 715 ± 10°.

The temperatures of beginning of the highest temperature stage of decrepitation, and shortest distances of the specimens from the granite contact, are shown below in the table.

TABLE 1

Specimen	Distance from Contact	Temp. of D2
A	2100 ± 200 Feet	615 ± 10° C.
B	1550 ± 150	608 ± 20
C	100 ± 40	585 ± 20

Evidently there is no increase of the D2 temperature approaching the granite contact, and probably there is a decrease.

Yellowknife, N.W.T. Ten specimens of metamorphosed basalt, collected by R. W. Boyle along two east-west traverses in the vicinity of Yellowknife, were prepared in identical manner, including cleaning in hydrochloric acid, and were heated in the decrepitation apparatus with special precautions to keep all variables as constant as possible. The results are shown below in the table, which also includes the shortest horizontal distance of each specimen from the large granite batholith to the west, and brief petrographic notes.

Table 2

Line	No.	Decrepitation Temperatures			Dist. from Granite	Petrographic Notes
C	1	358±20	500±20	609±20	350 Feet	Amphibole, sodic plagioclase, quartz, magnetite.
C	3	398±20	(500)	623±20	2550	Amphibole, sodic plagioclase, epidote, magnetite.
C	5	360±30		668±20	4100	Amphibole, plagioclase, epidote-zoisite, carbonate
F	1		527±30	649±20	500	Similar to C 1
F	2	367±20	(530)	619±20	1200	Similar to C3 and C5
F	3	408±30		616±20	2000	
F	4	(450)		626±30	4000	
F	5	(317)		608±30	5000	
F	7a			659±20	6500	
F	9	411±10		664±20	9000	Chloritic, little amphibole.

Miscellaneous Tests. a) Granodiorite

A specimen of massive pinkish grey granodiorite from the Jervis Inlet area, B.C., was obtained from a suite collected by W. R. Bacon. It occurs along the south coast of Nelson Island. The mineral composition, including complex zoning of the plagioclase, has been described by Bacon (1952). While field evidence is not conclusive that this rock had an igneous origin, there are no contrary facts, and most field geologists would classify it as igneous by intuition.

Decrepitation was found to be very complex. A feeble stage began at 340±20°, and increased to a vigorous stage starting at 375±20°, with a peak rate near 450°. Another feeble stage began at 475±30°, and about 535° the quartz pre-inversion curve started to rise. There was a rapid rise and fall of rate at 575±10°. Two small increases in rate, not fully resolved, appeared between 585° and 660°. A vigorous stage began at 750±20°, with a peak rate near 775°. No other stage of decrepitation was evident to 1050°, except one of inversion or decomposition type at 970±20°.

Comparison of the decrepigraphs of para-gneiss and the above granodiorite indicated a general similarity, except that the highest temperature stage (D2)? is at a higher temperature in the latter case (635–710° for para-gneiss, 750° for granodiorite).

Miscellaneous Tests. b) Diabase

A specimen of diabase from a large dike was available in a suite collected by the writer from the south shore of Great Slave Lake, 26 miles west-south-west from the trading post of Snowdrift (Lat. 62°15′N, Long. 111°30′W). The specimen was taken 8 inches away from the contact which was found to contain a glassy selvage. Under the microscope, the grain size was found to be somewhat seriate, from approximately 0.5 mm to 0.02 mm. The largest crystals are 1) plagioclase, somewhat altered to an aggregate of unidentified minerals, and 2) pale greyish green pyroxene. Smaller crystals of plagioclase, pyroxene, bright green (pleochroic) amphibole, magnetite, and traces of quartz, carbonate and biotite are intimately intergrown. The crushed rock was treated with hot hydrochloric acid before heating.

Decrepitation was found to be too feeble to give a resolvable rate recording. An electronic scalar was attached to the ratemeter and the detected noises were totalled in 20° intervals. From these values were subtracted equivalent values obtained with no charge in the heating block. No significant residual was found up to 750°. This rock, undoubtedly igneous, has decrepitation characteristics very different from those of metamorphic rocks of similar chemical composition, *i.e.* greenstone and amphibolite.

DISCUSSION OF THE RESULTS

The decrepitation temperatures of the metamorphic specimens studied are shown in Table 3, classified tentatively as to the cause of each stage.

Too few specimens gave enough low temperature decrepitation (below 300°) to allow any quantitative generalizations to be made. However, the fact that hydrothermal minerals generally give vigorous decrepitation in this range, and also contain abundant multiphase fluid inclusions, while the reverse is true in the case of the metamorphic minerals, suggests that crystallization of the latter is not from aqueous solutions.

The peculiar D3 stage of decrepitation can be detected in most of the rate curves described above, but the meaning of this was not determined.

All of the specimens gave more or less vigorous high temperature decrepitation which started at 565° to 710°. The average value of the results from 17 localities is 633°, giving the mean of all values from one locality the same weight as single values. These results are quantitatively similar to those obtained with metacryst almandite garnet (Smith,

TABLE 3. SUMMARY OF RESULTS

Locality	Metamorphic Mineral or Rock	Probable Original Rock	Decrepitation Temperatures (° C.) D1	D2	D3	D4	Remarks
Barry Bay, Ont.	Hornblende Gneiss	Sediment	—	700 ± 20	340 ± 20	Quartz	
Barton Mine, N. Y.	Garnetiferous Hornblendite	—	—	606 ± 30	—	—	
Bobcaygeon, Ont.	Granite Gneiss	Sediment	216 ± 20	690 ± 20	320 ± 20	Quartz	Also 610 ± 20, and 440 ± 20.
Bracebridge, Ont.	Hornblende Gneiss	Sediment	(250)	705 ± 20	340 ± 20	Quartz	
Bryce Twp., Ont.	Hornblendite	Basalt	—	640 ± 20	—	—	Also 525 ± 30.
Cadillac, Que., A	Amphibolite	Basalt	—	581 ± 20	342 ± 20	—	
Cadillac, Que., B	Amphibolite	Basalt	—	620 ± 20	—	—	Also 425 ± 40.
Calumet Is., Que.	Amphibolite	—	—	652 ± 20	—	—	
Hybla, Ont.	Amphibolite	Sediments	—	625 ± 10	335 ± 20	—	Also 475 ± 20.
Lake Athabaska, N.W.T.	Hornblende Schist	—	—	595 ± 20	365 ± 25	Quartz	
Long L., Ont.	Amphibolite	—	133 ± 10	650 ± 20	333 ± 20	—	Near aplite
O'Connor L., N.W.T.	Garnet Gneiss	Shale	(255)	635 ± 20	(330)	Quartz	
O'Connor L., N.W.T.	Hornblende Gneiss	Basalt	—	632 ± 20	370 ± 10	—	
Renfrew, Ont.	Crystalline Limestone	Limestone	210 ± 30	615 ± 10	340 ± 30	Quartz	2100′ from granite.
Renfew, Ont.	Crystalline Limestone	Limestone	—	608 ± 20	355 ± 30	—	1550′ from granite.
Renfrew, Ont.	Crystalline Limestone	Limestone	275 ± 30	585 ± 20	365 ± 30	—	100′ from granite.
Snow L., Man.	Chlorite Schist	Diabase	—	565 ± 20	—	—	
Whitney, Ont.	Granite Gneiss	Sediment	—	710 ± 20	350 ± 20	Quartz	Also 440°.
Wilberforce, Ont.	Amphibolite	—	—	575 ± 20	332 ± 10	Quartz	Near pegmatite.
Willsboro, N. Y.	Garnet	Limestone	—	594 ± 10	(350)	—	Contact metasomatic rock.
Willsboro, N. Y.	Wollastonite	Limestone	—	581 ± 20	275 ± 20	—	
Yellowknife, N.W.T.	Amphibolite	basalt	—	634 ± 40	(375)	Quartz	

1952 b). In the case of garnet, it was shown that the rate of decrepitation of this stage is directly related to the abundance of crystalline inclusions. By analogy, but with less certainty, the D2 stage of decrepitation of the high grade metamorphic rocks is due to crystalline inclusions in the constituent minerals. If this is correct, it may further be assumed that the majority of the inclusions were trapped during the primary crystallization. The present tentative interpretation of the decrepitation rate curves is that the beginning of the D2 stage represents the temperature of this crystallization, correctable for the effect of pressure during crystallization.

Internally, the results do not conflict with the above interpretation. The lowest D2 temperature (565°) was found in a garnet-chlorite schist, and the highest (near 700°) were found in gneisses which probably would initiate a petrological dispute as to whether they are very high grade metamorphic or igneous rocks.

In two cases (Renfrew, Ontario, and Yellowknife, N.W.T.) no gradient of D2 temperature was found outward from the granite contact. Probably facts such as this will be important in theories of formation of granite, if the D2 stage of decrepitation represents the maximum temperature to which the rock was subjected during metamorphism and intrusion (or granitization). Interpretation will be reserved until more detailed studies have been made around other batholiths.

CONCLUSIONS

High grade metamorphic rocks from 17 localities have a stage of decrepitation beginning between 565 and 710°, with an average value of 633° C. These results are qualitatively and quantitatively similar to those previously reported for metacryst almandite garnet, and probably are due to misfit of crystalline inclusions in the constituent minerals when they are heated above the temperature at which they crystallized, or when they are heated above the maximum temperature which they have experienced.

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PLATINUM METALS IN SOME CANADIAN URANIUM AND SULPHIDE ORES

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Abstract

A spectrographic method has been developed for the quantitative analysis of the platinum metals in fire-assay beads obtained from both sulphide and some uranium ores to which gold is added as a collector. Beads are incorporated in lead buttons and analyzed using lead as a variable internal standard.

Results are given for several nickeliferous sulphide ores from both Canada and South Africa (Insizwa), for an exceptional type of uranium ore, and for non-nickeliferous copper sulphide ores of both Precambrian and post-Cambrian age. The amounts of Pd, Pt, Rh, Ru, Ir, and Os are given in ppm, and ratios of these are compared with those noted by Rankama & Sahama for a composite of magmatic sulphides. A comparison is also made of the distribution of the platinoids in different metallic minerals.

Spectrographic investigation of the platinum metal content of various Canadian ores was initiated some time ago in order to complete mineralogical studies of nickeliferous ores in Canada. A technique involving the use of fire-assay beads and the incorporation of these in mercury-gold beads for spectrographic analysis, using gold as an internal standard, has been previously described. (Hawley, Lewis & Wark, 1951). Further investigation of this method uncovered difficulties in the uniform mixing of platinum and rhodium "black" and of bismuth in the gold amalgam which in turn gave rise to the development of a new technique by which fire assay beads of precious metals are dissolved in lead, a method to be described in detail elsewhere.[1]

This spectrographic method has now been applied to the study of platiniferous uranium ores, following a suggestion by Dr. G. S. Hume, Department of Mines and Technical Surveys, in 1950, and the study has been extended, first to include the nickeliferous sulphides of the Sudbury district and the non-nickeliferous sulphides which occur in scattered deposits between Sudbury and Sault Ste Marie, Ontario, with the thought in mind of attempting in this way to delimit metallogenic provinces characterized by the platinum metals. The study was later expanded to include other nickeliferous and non-nickeliferous sulphide ores, as well as samples from gold and mixed, base-metal ores of both Precambrian and post-Cambrian age. Though by no means complete, the results obtained to date are presented herewith and some tentative conclusions are given.

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[1] Trans. Can. Instit. Mining & Metal., vol. **56**, pp. 19–26, 1953.

LEAD BEAD METHOD OF SPECTROGRAPHIC ANALYSIS OF PRECIOUS METALS AND BISMUTH

Since this method is being described elsewhere in greater detail, only a summary will be included here.

Fire-assay beads are made from one assay ton, or a fraction thereof, of the selected ore or ore minerals. In those samples which do not contain much if any gold or silver, pure gold is added to the sample as a collector prior to assaying, the amount of which may be varied from 1 to 10 mg., particularly to insure the production of a weighable bead. Losses on assaying, due to volatilization and absorption in cupels, have so far not been corrected.

Resultant precious metal beads are then fused with chemically pure lead with a blowpipe on charcoal[1] and the weight of lead actually added is determined from the total weight less the known weight of assay bead. The amount of lead used is within the ratio of 9 to 9.9 parts of lead to 1 to 0.1 part of precious metal bead. Lead buttons so formed, depending on their size, may be used in whole or in part. These are then soldered on the top of 2 inch lengths of 1/16″ to 1/4 dia. copper electrodes. Where increased sensitivity is required, two such electrodes are prepared as anode and cathode: otherwise hemispherical-tipped graphite counter electrodes have been used.

Samples are then sparked with a high voltage condensed spark (ca 15,000 v.) supplied by a Hilger unit, for 1 minute. Slit —60 microns, Gap —2 mm., Transmission —100%, Film type—Spectrum Analysis #1.

In order to prepare working curves, standards were made up containing Pd, Au, Ag, Pt, Rh, Ru and Ir as well as Bi since the latter is almost invariably present. As gold and silver may be major constituents compared with the other precious metals, in most samples standards of these were prepared covering a range of 0.001 to 10% Au or Ag %Pb and working curves were established using four different gold and silver lines.

Throughout lead is used as an internal standard and intensity ratio of *element line/lead line* is plotted against the calculated ratio of *% Element/% lead*, a method referred to as the "Mutual Standard" method by Churchill & Russell (1945) and discussed by Harvey (1950), and Coulliette (1943).

Having determined the ratios of percentage of each element to percentage of lead, (from the working curves) the percentage lead is then calculated according to

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[1] An alternative method recently used is to carry out the fusion in graphite cups in-inserted in a small furnace under hydrogen with maximum loss of 0.1% lead.

$$\%\,\mathrm{Pb} = \frac{100}{1 + \frac{\%\,\mathrm{Au}}{\%\,\mathrm{Pb}} + \frac{\%\,\mathrm{Ag}}{\%\,\mathrm{Pb}} + \frac{\%\,\mathrm{Pd}}{\%\,\mathrm{Pb}} + \frac{\%\,\mathrm{Bi}}{\%\,\mathrm{Pb}} + \text{etc.}}$$

The figure for %Pb should check the actual known amount of lead added. A slightly higher percentage may be present if any lead has been left in the original precious metal assay bead, but on the whole excellent checks have been obtained.

Knowing accurately the percentage lead, the percentage of the sought-for element is then found by simply multiplying

$$\frac{\%\,\text{Element}}{\%\,\mathrm{Pb}} \times \%\,\mathrm{Pb}$$

Percentage element may then be stated in terms of milligrams per assay ton or troy ounces per ton, knowing the weight of the lead plus precious metals button. In this paper results are stated in terms of grams per metric ton or parts per million, except where noted. Since this work was completed Treadwell, Amrein & Bodmer (1952) have reported spectrochemical analysis of silver in lead over the ranges of 0.001% to 1.6% with deviations of 5% or less. Ageing of the lead silver alloys over a period of six weeks has shown that original homogeneous solid solutions ex-solve silver crystals along grain boundaries and yield less dense lines on excitation with an interrupted spark discharge. This is clearly a feature which requires consideration, not only for silver but for the other metals included in the present investigation and is undergoing further study.

Some measure of the accuracy obtained by this method is given by the following results on gold and silver beads in which only traces of the platinum metals were found by dc arc qualitative methods:

TABLE 1

	Gold		Silver		% Difference	
	mg. Assay	mg. Spectro	mg. Assay	mg. Spectro	Au	Ag
Q-1	11.81	11.89	3.1	2.37	0.7	20.
Q-2	11.98	11.93	2.65	2.70	0.45	1.9
P-1	476.00	515.40	1658.43	1622.50	8.3	2.5
P-2	476.05	477.20	1658.43	1658.20	0.3	0.1
P-3	476.01	477.60	1658.43	1653.07	5.37	0.3
C-1	18.10	16.45	57.55	57.01	9.0	1.0
C-3	17.345	14.16	64.45	64.96	18.0	0.8
C-4	17.185	18.18	64.45	62.80	5.7	2.5

Though no analyzed samples containing the platinum metals have been available, prepared standards were made independently and with different dilutions in lead, and found to check satisfactorily the working curves previously established. In addition special lead beads were made by evaporating, in lead cups, solutions containing known amounts of Pd, Pt, and Rh. Table 2 gives a comparison of spectrographic determinations with actual amounts of the metals in a prepared standard.

TABLE 2

	Pd	Pt	Rh
Amount in Standard—mg.	0.021	0.0350	0.0210
Amount determined spectrographically—mg.	0.021	0.0330	0.0214

The range covered by our analytical curves for the platinum metals is from 0.00056% to 3% and for gold and silver up to 10% of the lead beads.

According to this technique there is theoretically almost no limit to the lower limit of detectability of platinum metals since by concentrating these from several assay tons the actual amount may be eventually brought up to a level which is detectable spectrographically. Practically, however, if the gold or silver present, or added as a collector, increases too greatly, the platinum metals may be diluted too much for actual detection. Detectability of platinum, in terms of the final lead bead is 0.00175%, and of palladium and rhodium 0.0005%. Using one assay ton of mineral or ore, and a lead bead of 10 mg. these percentages give a detectability of platinum of about 0.003 ppm. and of palladium and rhodium of 0.0008 ppm.

Curves for ruthenium and iridium, in contrast to the others cover only the range from 0.2% to 2.0% in lead beads. These metals were only determined in a few cases in the later stages of the investigation by concentrating them in smaller lead beads than were used for determining the other platinoids. Amounts recorded in three samples fall below the above limit and hence will require further checking. Amounts of osmium given are only approximations based largely on the fact that its sensitivity is recorded as equal to iridium. Since both ruthenium and osmium form volatile oxides, our results must be regarded as tentative, awaiting more accurate techniques for their concentration by wet methods rather than by fire-assay.

PLATINUM METALS IN URANIUM ORES

Table 3 gives the analyses of platinum metals in two uranium ores, one a phenomenal type from Lake Athabasca, the other from Great Bear Lake, for comparison.

In the ore from Athabasca exceptional concentrations of the platinum metals are present, the ratio of Pd: Pt: Rh approximating 6:1:0.01. Due to lack of unground specimens it has not been possible to separate individual minerals for analysis, but there does appear to be some correspondence between the amount of gold and amounts of platinum metals as indicated by the low and high values, given. This confirms an opinion by S. C. Robinson,[1] who identified the following minerals in this ore: —pitchblende, tiemannite, galena, pyrite, chalcopyrite, niccolite and gold.

As a matter of curiosity following the above determinations, concentrates of niccolite, cobalt arsenides (skutterudite and safflorite) and a composite sample consisting largely of pitchblende from a deposit at Great Bear Lake were analyzed in a similar manner, but only the very small amounts of palladium and rhodium indicated were found.

Though considerable quantities of palladium are known in mixed arsenides at Sudbury (see p. 469) there is obviously no constant association of these metals with such minerals. Furthermore no data are available to indicate any direct relation between the platinum metals and the uranium oxides in such ores.

TABLE 3. PLATINUM METALS IN URANIUM ORES

Grams per Metric Ton

Deposit	Minerals	Palladium	Platinum	Rhodium	Others
Athabasca (Nicholson)	Ore	0.10–443.	.02–73.	.006–.67	Au—25–2242. Ag—17–209. Ru—0.35* Ir—0.43 Os—0.33 (?)
Great Bear Lake Area	Niccolite (calcined)	.03–.045	tr	tr	Ag—56–74.
	Cobalt Arsenides (calcined)	.05	tr	.037	Ag—245.
	Composite Ore (calcined)	tr	—	—	Ag—2543.

* Ru, Ir, Os, determined approximately on only one sample, but show in three separate beads of this sample.

PLATINUM METALS IN NICKELIFEROUS SULPHIDE ORE MINERALS

The results of spectrographic analyses of selected minerals in nickeliferous ores are given in Table 4. In all cases the specimens contained no visible platiniferous minerals, thus the results do not indicate maximum amounts of such elements in the ores as a whole. Several of the analyses do show, however, an erratic distribution of palladium and platinum which may best be accounted for by inclusion of discrete mineral particles of these elements, as in chalcopyrite, pentlandite and arsenides.

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[1] Written communication.

Samples analyzed consist of concentrates from various localities along the south range of the Sudbury basin, from the base metal ore of the Treadwell-Yukon, within the basin, and from chalcopyrite associated with pyrrhotite and pentlandite in the Springer deposit of Baldwin township on the west. In addition are given results on samples of the recently discovered nickeliferous sulphides at the base of the Duluth gabbro, Minnesota and of samples from Lynn Lake, Manitoba, Rankin Inlet on the west coast of Hudson's Bay, and of a suite of samples obtained from the magmatic deposit at Insizwa, South Africa. For comparison, similarly stated ratios given by Rankama & Sahama (1949) are presented for a composite of magmatic sulphides.

The occurrence of the platinoids in ores from Sudbury is, of course, well known and these will be further discussed. The presence of the three platinum metals in the Treadwell-Yukon sample containing chiefly pyrite with minor galena and sphalerite, may be taken as a very likely indication of a genetic relation between this ore and those on the margins of the Sudbury basin. Scattered sulphide deposits west of Sudbury fall into two categories, those with pentlandite and those without. The Springer deposit in Baldwin township and the Shakespeare mine, west of Sudbury are both nickeliferous and carry the platinum metals. Others, which are non-nickeliferous are reported with such ores later (see p. 472).

Deposits farther afield, such as those of the Duluth gabbro, Lynn Lake, Rankin Inlet, and Insizwa again illustrate the association of these metals with nickeliferous ores and give an approximation at least of the relative quantities present.

With few exceptions all of the samples analyzed show one or more parts per million of palladium and in many cases much more. Platinum and rhodium[1] are usually lower. Though chalcopyrite on the whole shows more of the platinoids, particularly palladium, this is not always the case, both pentlandite and pyrrhotite, as well as mixed arsenides, being locally richer in this respect. There is thus no very clear relation between the amounts of platinum metals, particularly of palladium and platinum, and the order of introduction of the common sulphides, though analyses to date do suggest ruthenium, iridium and osmium may possibly be concentrated more in pyrrhotite, usually the earliest of the three sulphides.

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[1] *Rhodium* was not determined in several samples due to use of a different technique employed at the time.

TABLE 4. PLATINUM METALS IN NICKELIFEROUS SULPHIDE ORES
Grams per Metric Ton

Sudbury	Mineral	Palladium	Platinum	Rhodium	Others
South Range	Pyrrhotite	0.45	0.18	0.10	Ru 0.35–0.04
		0.75	0.85	0.45	Ir 0.33–0.02 Os 0.37 (?)
South Range	Chalcopyrite	1.17	1.30	.27	
Falconbridge[1]	Chalcopyrite	34.28	1.54	nd	
Falconbridge	Chalcopyrite	1.61	3.77	nd	
Falconbridge	Pentlandite	17.50	29.8	nd	
Falconbridge		12.65	34.2+		
Falconbridge	Pyrrhotite	34.2+	15.6	nd	
		0.13	0.170		
Falconbridge	Arsenides	246.8	tr	nd	
Falconbridge	Pyrite	0.31	0.37	nd	
Nickel Offsets	Pentlandite & Pyrr.	2.00	2.68	0.10	
Treadwell-Yukon	Py. Ga. Sp.	1.92	0.61	1.73	
Springer-Baldwin	Chalcopyrite	0.03		0.04	
Duluth Gabbro	Pyrrhotite	1.47	0.11	0.07	
Lynn Lake Man.	Pyrrhotite	1.36	0.18	0.018	
Rankin Inlet N. W. T.	Pyrrhotite	3.79	1.26	0.55	
	Pyrrhotite	4.45	2.40	.30	Ru 1.6, Ir 1.03
	Pyrr. Pent. Cpy.[3]	5.15	2.71	0.58	Ru 2.12, Ir 1.03 Os 1.0 (?)
Insizwa, S. Africa	Chalco-cubanite	13.75	2.06	0.057	Ru .09
	Pyrrhotite-Pent.	0.38	0.48	0.38	Ru .41, Ir .51 Os .34 (?)
Magmatic[2]	Sulphides	4.0	2.0	0.3	Ru 1.0 Ir 0.4 Os 0.1

[1] After Hawley, Lewis & Wark, Econ. Geol. **46**, pp. 149–161, 1951.

[2] Noddack, Ida & Walter, Zeit. Physik. Chem. A. **154**, 207, and Rankama & Sahama-Geochemistry, 1949, pp. 692.

[3] Sample dominantly pyrrhotite with minor pentlandite and chalcopyrite.

Abbreviations—Py pyrite, Pyrr. pyrrhotite, Ga galena, Sp sphalerite, Pent. pentlandite, nd Not determined.

Little information is available regarding the ratios of the various platinum metals, one to another, in ores from which they have been recovered. Actual recovery is of course not necessarily the same as actual occurrence in the ores and individual minerals, so basic data on the ratios of these metals in the ore minerals themselves are badly needed. Analyses of a composite of magmatic sulphides, from various localities, in part Norwegian, were made by Noddack & Noddack (1931) and are quoted by Rankama & Sahama (1950). In these the ratio of Pd:Pt:Rh, in parts per million is 4.0:2.0:0.3, and that of Ru:Ir:Os is 1.0:0.4:0.1.

It is not possible to arrive at an average ratio from our figures for the Sudbury area, though it may be noted that for nine pyrrhotite samples from the south range, the Pd:Pt:Rh ratio is 4.0:2.0:1.3. Actual quantities are lower than given by Rankama, but the Pd:Pt ratio agrees with his, while that of rhodium is somewhat higher.

Attention may also be called to the close similarity between the relative amounts of Pd, Pt, and Rh in the pentlandite-pyrrhotite ores of Rankin Inlet and the composite given by Rankama & Sahama, an average of the three samples from this locality giving a ratio of Pd:Pt:Rh of 4.16:2.0:0.4.

The magmatic ores of Insizwa, described and classified by Scholtz (1936) are divided into three groups, massive chalcopyrite-rich ore containing much cubanite, massive pyrrhotite-rich ore with intergrown pentlandite, and disseminated ore. Samples from the first two were analyzed for individual platinum metals and the totals are compared in Table 5 with recalculated assays on two and three samples respectively, given by Scholtz.

Table 5. Total Platinoids Insizwa Ore

Grams per Metric Ton

	Spectrographic	Scholtz—Assays
Pyrrhotite ore.	2.5	6.85– 7.71 (2)
Chalcopyrite ore.	17.01	11.15–46.3 (3)

Our results thus fall within the range given by Scholtz for the chalcopyrite-rich ore, but are lower than his for pyrrhotite.

A study of our results, given in Table 4, shows in addition to the fact that more platinoids are concentrated in the Insizwa chalcopyrite, that chalcopyrite contains between three and four times as much palladium and platinum as the pyrrhotite ore and about seven times as much silver. The pyrrhotite ore, however, contains about six times as much rhodium and over four times as much ruthenium as found in the chalcopyrite. Iridium and likely an equal amount at least of osmium are also present in the pyrrhotite but were not detected at all in chalcopyrite ore.

Ratio of Pd:Pt:Rh in Insizwa pyrrhotite ore is about 1 and in chalcopyrite, about 14:2:0.06. An average of the two ores (though it is not clear that they are present in equal amounts) gives a ratio for these metals of about 10:2:0.3 in which Pd is much higher than given by Rankama & Sahama, but, surprisingly, the figures for platinum and rhodium are identical with theirs. It is apparent however, that to obtain dependable ratios of these metals for various types of nickeliferous ores many more analyses are required.

Only in our more recent work have results been obtained on the distribution of what are normally thought of as the somewhat rarer platinoids, namely ruthenium, iridium and osmium. As is well known, the platinum metals fall in *two* groups according to their atomic numbers and properties, Ru, Rh, and Pd, and Os, Ir, and Pt, and one might expect some such association in nature. So far however, this cannot be clearly demonstrated. For instance, in the Insizwa ore high palladium in chalcopyrite is not accompanied by high ruthenium, and in *one* sample of pyrrhotite of the same ore, low platinum is accompanied by relatively high iridium as well as ruthenium and rhodium.

On the other hand, as will be seen later, in Table 6 of the non-nickeliferous ores, some samples contain both rhodium and palladium, members of one triad, but no platinum.

In Table 4, of the nickeliferous ores, ruthenium, iridium and osmium were only determined in three different ores. Results of the Insizwa ore have already been mentioned. In the other two, again Ru, Ir and Os are present as at Insizwa, in pyrrhotite-rich ores. Rankama & Sahama give the ratio and parts per million of these metals as Ru:Ir:Os = 1.0:0.4:0.1, for a composite of magmatic sulphides apparently from Norway. In contrast, our results for both Sudbury pyrrhotite and Insizwa pyrrhotite-rich ore show more nearly equal quantities of these three metals though about the same total of slightly over 1 ppm. The Rankin Inlet sample on the other hand, shows a total of over 4 ppm, with ruthenium about double that of iridium and of osmium. Again, much further study is required as well as different concentration techniques to satisfactorily arrive at reliable ratios for these metals.

PLATINUM METALS IN NON-NICKELIFEROUS SULPHIDE ORES

Spectrographic analyses of minerals in non-nickeliferous sulphide ores of Precambrian age are given in Table 6. These include chiefly copper ores in Quebec, Ontario, Manitoba, two gold deposits, as well as arsenides from the native copper deposits of Michigan.

In view of the fact that research on the platinum metals in their nearly pure state was carried out in our laboratory at the same time as this work, the possibility of contamination of samples was carefully examined. As a check against several of our determinations, qualitative analyses of gold beads prepared from several of the ores here described, were kindly undertaken by Dr. B. J. Stallwood, Mines Branch, Dept. of Mines and Technical Surveys, and confirmation was obtained of the presence of Pd, Pt, Rh, and Ir and Ru in several of these.

In the northwestern Quebec area the related deposits of Noranda, Quemont, Waite, Aldermac and Normetal almost all contain some of the platinum metals in determinable amounts, with palladium in excess of platinum. In two instances, rhodium is in excess of palladium. In the Noranda and Aldermac ores palladium increases with the order of paragenesis, namely pyrite, pyrrhotite, chalcopyrite, though in both the Normetal and Flin Flon (Man.) deposits amounts of this metal are about the same in both pyrrhotite and chalcopyrite. In the latter, rhodium is again slightly in excess of palladium.

Table 6. Platinum Metals in Non-Nickeliferous Sulphide Ores

Grams per Metric Ton

Deposit	Mineral	Palladium	Platinum	Rhodium	Others
Quebec					
Noranda	Chalcopyrite	.025–.018	tr	tr—.055	Ru—tr
	Pyrrhotite	.017			
	Pyrite	.012	tr	tr	
Waite	Pyrrhotite	.016	tr	tr	
Quemont	Chalcopyrite	tr	tr	tr	Ru-Ir-Os—tr
Aldermac	Chalcopyrite	1.03	.09	tr	
	Pyrrhotite	.02		.06	
	Pyrite	tr		.003	
Normetal	Chalcopyrite	.004		.003	
	Pyrrhotite	.004			
Opemisca	Chalcopyrite	.02			
Powell-Rouyn	Pyrite	tr	tr	tr	
Manitoba					
Flin Flon	Chalcopyrite	.055		.07	
	Pyrrhotite	.056			
Ontario					
North Shore Lake Huron—					
Bruce Mines	Chalcopyrite	.019	tr	.021	
Bi-Ore	Chalcopyrite	tr	tr	.13	
Bald Dome	Chalcopyrite	tr	tr	.08	
Eckett	Chalcopyrite				
Rock Lake	Chalcopyrite	.033	tr	tr	
Porcupine Dist					
Hollinger	Pyrrhotite	.006		.03	
Michigan					
Keweenaw Pen.	Cu Arsenides	.068	.041		

tr=trace, found on qualitative analysis.

In chalcopyrite from the scattered, small, non-nickeliferous deposits along the north shore of Lake Huron, platinum metals are also present in either traces or detectable amounts with one exception. Again palladium is in excess of platinum and rhodium in excess of palladium. Total amounts of the platinoids in these ores, where pentlandite is absent is very much less than in those ores containing even small amounts of nickel.

The occurrence of traces of these metals in pyrite from the Powell-Rouyn gold vein, near Noranda, and of minute amounts of palladium and rhodium in pyrrhotite from the Hollinger gold deposits are of interest in showing their rather ubiquitous character. Similarly the presence of palladium and platinum in a concentrate of algodonite from the Keweenaw peninsula, Michigan, in which nickel and cobalt are also prominent as trace elements, suggests these metals are by no means as rare as might be supposed. Whether they are of genetic significance, however, is still a question, but attention is called to the results already given for nickeliferous sulphides at the base of the Duluth gabbro, an intrusive believed similar to gabbro to which the Keweenawan copper ores have been ascribed.

On the whole, though it was first thought that the presence of platinum metals in various copper ores both in Quebec and Ontario might indicate a genetic relation to the Sudbury ores, both the decidedly lower concentrations in non-nickeliferous ores and the demonstrated ubiquitous character of the metals in even unrelated gold deposits, precludes the drawing of any such conclusions at this time. Since nickel is so much more readily determined, the delineation of any nickeliferous and platiniferous metallogenic provinces can obviously be made more simply by determination of nickel.

PLATINUM METALS IN POST-CAMBRIAN SULPHIDES

As a sequel to the above studies a few analyses have been made on chalcopyrite concentration from post-Cambrian (Palaeozoic) ores in Newfoundland and the Eastern townships, Quebec. These are given in Table 7.

In these ores the presence of only traces of palladium in Newfoundland

TABLE 7. PLATINUM METALS IN POST-CAMBRIAN CHALCOPYRITE
Grams per Metric Ton

	Palladium	Platinum	Rhodium
Newfoundland			
Buchans	.026	tr	tr
Quebec			
Ascot	1.82	.041	tr
Ascot	1.61	.062	
Moulton Hill	0.16	tr	tr
Weedon	0.65	.410	tr
Weedon	0.34	tr	

chalcopyrite and of both palladium and platinum in the Quebec deposits is noted. In the latter palladium averages nearly 1 pm and the ratio of Pd:Pt averages 9:1, a somewhat higher ratio of palladium than in Precambrian ores. The absence of rhodium may also be a characteristic difference of such ores, but again more detailed studies will be required to determine reliable ratios of the platinoids in post-Cambrian sulphides of other areas.

SUMMARY AND CONCLUSIONS

By means of fire-assay beads in which gold is used as a collector, a satisfactory spectrographic technique has been established for the determination of the platinum metals quantitatively in both uranium and sulphide ores and ore minerals. Beads are diluted in lead, mounted on copper electrodes, and with a high voltage condensed spark, ratios of percentage precious metals to percentage lead are determined by the "Mutual Standard" method. Gold, silver and bismuth may be similarly determined. By controlling the amount of gold and lead and varying the fractions or number of assay-ton samples used the method may be applied to minerals with a wide range of concentrations of the precious metals.

Uranium ore from one locality in the Lake Athabasca area contains remarkable concentrations of the platinum metals which appear to bear a rough relation to the amount of gold present. In this ore the ratio of Pd:Pt:Rh is 6:1:0.01; while Ru, Ir, and Os are present in about equal proportions and in amounts up to 0.3 ppm. each. Tests on uranium ore from Great Bear Lake indicate three to four hundredths of a part per million of Pd and Rh in nickel and cobalt arsenides.

Analyses of nickeliferous sulphides from various areas in Canada are compared with the platinoids in similar ore from South Africa and with ratios of these given by Rankama and Sahama for a composite of magmatic sulphides.

All nickeliferous ores tested indicate the presence of platinoids. All contain 1 or many ppm. palladium and usually platinum and rhodium in lower quantities. Of the sulphides, chalcopyrite is the richest in platinum metals, but pentlandite and pyrrhotite may be equally so. There is a suggestion that ruthenium, iridium and osmium are concentrated more in the earlist mineral, pyrrhotite.

Though no definite ratios of Pd:Pt:Rh can be given for Canadian ores as a whole, the Pd:Pt ratio of some Sudbury pyrrhotite is the same as given by Rankama and Sahama though amounts are less, while rhodium is greater. Ratios for the three metals in an average of Rankin Inlet ore are almost identical with figures given by Rankama and Sahama as are the parts per million.

In the Insizwa magmatic ore Pd and Pt appear concentrated in chalcopyrite while Rh, Ru, Ir and possibly Os are more abundant in pyrrhotite.

The average ratio of Pd:Pt:Rh of this ore shows more Pd but similar amounts of Pt and Rh, compared with the ratio given by Rankama and Sahama.

In non-nickeliferous copper-iron sulphides of Precambrian deposits palladium, rhodium and in a few cases, platinum are present in amounts ranging from 4/1000 to one ppm. Palladium is invariably present in larger amounts than platinum, but in several cases, peculiarly, rhodium is in excess of palladium. In chalcopyrite of base metal ores of Palaeozoic age, palladium and platinum have both been detected, ranging from about 3/100 to nearly 2 ppm. with palladium always in excess of platinum.

The much greater affinity of these metals for nickeliferous ores is amply borne out by the data presented. Since the determination of nickel is less difficult than of the platinoids, delineation of metallogenic provinces can be made most easily by the former.

Though, according to Goldschmidt's geochemical classification of elements, all the platinoids are noted as *siderophile* in character (most readily soluble in molten iron and nickel), and Pd, Pt, and Ru are classified also as being concentrated but to a lesser extent with the chalcophile elements (having an affinity for sulphur, Rankama & Sahama 1949, p. 88), rhodium, iridium and osmium may likewise be so classified in view of their frequent presence in pyrrhotite. The persistence of traces of the platinum metals in pyrite of hydrothermal gold deposits is also shown.

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STUDIES OF RADIOACTIVE COMPOUNDS: VI—META-URANOCIRCITE[1]

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Abstract

Meta-uranocircite from Falkenstein, Saxony is tetragonal with a 6.96, c 16.90 A; space group $P4/nmm$; cell contents near $2[Ba(UO_2)_2(PO_4)_2 \cdot 8H_2O]$. A second, laboratory-prepared hydrate is tetragonal with a 6.96, c 17.57 A; space group $P4_22$; cell contents probably $2[Ba(UO_2)_2(PO_4)_2 \cdot 10H_2O]$ and not isostructural with autunite.

A specimen from Madagascar shows optical and structural properties which vary between those of meta-uranocircite and meta-autunite indicating that an isomorphous series exists between the two minerals.

The decrease in c with increase in ionic radius of the contained cation in the meta-phosphates is thought to be due to the function of water within the hydrates. The increase in c with increase in ionic radius of the cation in the fully hydrated phosphates suggests that the cations occupy the (b) rather than the (a) positions in Beintema's structure. The stability of the fully hydrated structure increases with decrease in the ionic radius of the cation.

Meta-uranocircite is a hydrous Ba U phosphate. It is known to be one of a number of naturally occurring phosphates and arsenates with the general formula $A(UO_2)_2(XO_4)_2 \cdot nH_2O$ where A is Cu, Ca, Ba, Mg or HAl and X is As and or P. These minerals form two structurally related groups known as the Torbernite and Meta-torbernite groups. In the Torbernites n varies zeolitically between 8 and 12 while in the Meta-torbernites n is 8 or less. For certain of the species the transition between the hydrates takes place near room temperatures and at low humidities and hence where the crystal development is poor, it is not known if the meta-types are of primary formation or are secondary dehydration products.

Beintema (1938) has pictured Ca-torbernite, that is autunite, as consisting of PO_4 tetrahedra and deformed UO_6 octahedra which are linked into two-dimensional sheets situated parallel to (001) (see Fig. 1a). The UO_6 octahedra deviate alternately upward and downward from the plane of the P atoms within the sheet and since adjacent sheets are related by a mirror plane, large cavities exist between the sheets. According to Beintema, water molecules and Ca atoms occupy the cavities. The lattice is body-centered. During the transformation to meta-autunite, the individually unchanged sheets are moved over a distance $[\frac{1}{2}\frac{1}{2}0]$ with respect to each other, permitting the sheets to lie more closely together and thus eliminating the large cavities (Fig. 1b). The lattice dimensions in the plane of the sheets remain unchanged but the distance between adjacent sheets is diminished from 10.35 to 8.47 A. The large body-centered lattice is transformed into the two primitive lattices of meta-autunite and the *c* dimension normal to the sheets is reduced from 20.70 to 8.47 A.

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[1] Extracted from a thesis for the Ph.D. degree, University of Toronto 1951, entitled *A study of certain uranium-bearing minerals and compounds* by I. H. Milne.

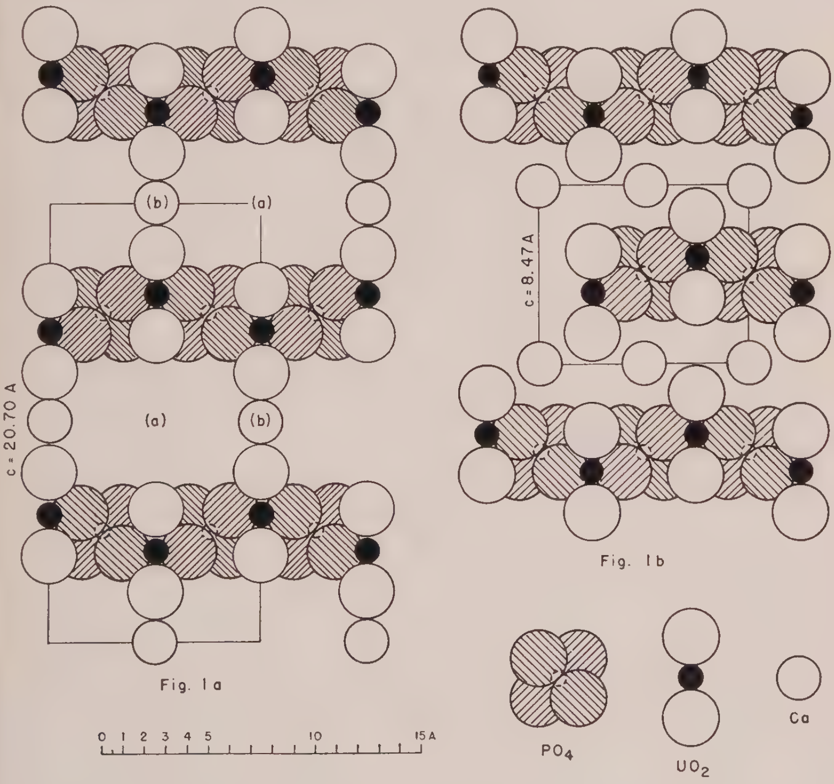


Fig. 1a

Fig. 1b

FIG. 1. The structure of autunite (1a) and meta-autunite (1b) projected on (110) (*modified from Beintema, 1938*). Half of the Ca positions are occupied in meta-autunite; all are occupied when the cation is monovalent.

A specimen labelled uranocircite from Falkenstein, Saxony in the form of an irregular intergrowth of yellow foliated crystals was available for this study. A spectrographic analysis kindly carried out by Mr. D. A. Moddle, Provincial Assayer for the Ontario Department of Mines, showed that the mineral consists essentially of Ba, U and P. Microchemical tests confirmed these results and indicated that the material is relatively free of calcium. The crystals although distorted, are obviously platey with a perfect cleavage parallel to the platey development. Two good cleavages at right angles to each other and normal to the platey development are also evident. In the chosen orientation the three cleavages were later designated (001), and (100) tetragonal prismatic respectively. The mineral has a hardness of 2 and is brittle. The specific gravity was determined with the aid of Clerici's solution to be 4.08. These properties are generally in agreement with those recorded by previous writers with the exception of the specific gravity; Weissbach (1877, in Dana, 1951, p. 987) obtained a value of 3.53.

COMPOSITION

The original analysis of uranocircite by Winkler, quoted by Weissbach, indicated the formula $BaO \cdot 2UO_3 \cdot P_2O_5 \cdot 8H_2O$ or $Ba(UO_2)_2(PO_4)_2 \cdot 8H_2O$. Partial analyses by Church (1877) confirmed the water content. Fairchild (1929) produced an artificial uranocircite with 6.1 molecules of water.

Church discovered that the water content varies readily with the humidity and temperature. He found that 4 molecules are lost at low temperatures (9–16° C.) under the water vapour pressure of strong sulphuric acid, a further 2 molecules are lost at 100° C. in air and the remaining two are driven off at red heat. Beintema continued this course of investigation by preparing a dehydration curve for artificial uranocircite with water content plotted against water vapour pressure. He found three distinct hydrates stable under certain conditions of water vapour pressure. The stable conditions for these hydrates with water vapour pressure translated into per cent humidity at 20° C. are given below.

Hydrate	*Water vapour pressure*	*Humidity*
$10H_2O$	Above 11 mm. Hg	Above 63%
$6H_2O$	Between 1 and 5 mm. Hg	Between 6 and 20%
$2H_2O$	Below 0.5 mm. Hg	Below 3%

It is apparent that analyses of specimens will vary with the locality of the laboratory and the time of year. The usual range of 30 to 50% humidity in the average museum or laboratory would result in a hydrate with water content intermediate between $10H_2O$ and $6H_2O$. It is therefore quite logical that Winkler's analysis and Church's partial analyses should show $8H_2O$. The loss of $4H_2O$ as recorded by Church when the material is dehydrated over strong sulphuric acid is also compatible with Beitema's dehydration data. The vapour pressure of strong sulphuric acid (density 1.74) with respect to water at 20° C. is 0.6 mm. Hg (Hodgman 1945, p. 1878), a condition which falls in the transition range between the hydrate with $6H_2O$ and that with $2H_2O$. Thus the product of dehydration over sulphuric acid could be expected to retain approximately 4 molecules of water after a loss of $4H_2O$. A further two would be lost at 100° C. in air and the remaining two at red heat, exactly as recorded by Church.

X-RAY STUDIES

Material under atmospheric conditions

The material under atmospheric conditions may be presumed to contain approximately $8H_2O$ from a consideration of humidity and temperature conditions within the laboratory and from the chemical work of Winkler and Church.

Cleavage fragments are anisotropic as seen lying on the cleavage surface (001). Most of these plates show a "microcline type" of twinning in two directions at right angles, parallel to (100) and (010). The extinction position of individuals is not quite parallel to the twinning planes and was found to vary up to 6° to these directions. The twin lamellae all have the same index of refraction in a direction approximately 45° to the twinning planes. Small flakes showing no twinning or only a minor amount of twinning, give a good biaxial interference figure with 2E varying from 10 to 45°. The two indices of refraction in the plane of the plates were measured in Na light and are compared below with the optical data obtained by Larsen (1921) on material from the same locality.

	Nuffield & Milne	*Larsen*
$X=c$	—	1.610
Y	1.621	1.623
Z	1.622	1.623
Sign	neg.	neg.

Rotation and Weissenberg films were obtained by rotating twinned and untwinned fragments about the edge between the basal and the prismatic cleavage. Despite the biaxial optics, a geometrically tetragonal cell was obtained which showed that the fragments had been rotated about the a axis in the chosen orientation. A second set of films about the other a axis was identical with the first. It is probable that the twinning observed optically is an indication of an irregular arrangement of water molecules and does not represent a true twinning of the structure.

For comparison, single crystal x-ray films were obtained for the chemically and physically similar minerals, meta-torbernite I and meta-autunite I. Meta-torbernite from Cornwall, England has uniaxial positive optical properties. Two specimens of meta-autunite I, one from Sosa, Saxony and the other from Autun, France both show a faint birefringence in the plane of the plates although in each case the two indices in the plane of the plates are sensibly the same. Both are optically negative and show a very small 2V. The extinction direction in the Sosa specimen corresponds to a diagonal in the tetragonal plates, while in the Autun specimen it is parallel to (100) or (010). Single crystal x-ray films of the two optical types are nevertheless identical and these films as well as those of meta-torbernite lead to tetragonal cells. Evidently the optical properties are extremely sensitive to the water content and to the distribution of the water molecules within the structure.

The zero-layer Weissenberg films with $a[100]$ as the rotation axis of meta-torbernite I, meta-autunite I and the uranocircite specimen are remarkably similar except that there are extra, rather weak diffraction spots in the latter film which result in exactly doubling one of the dimensions of the cell:

	Meta-torbernite I	*Meta-autunite I*	*Meta-uranocircite*
a	6.96 A	6.96 A	6.96 A
c	8.64	8.47	16.90[1]

[1] Frondel (1951a, p. 674) states: "The [sabugalite $HAl(UO_2)_2(PO_4)_2 \cdot nH_2O$] pattern cannot be completely indexed in terms of a cell with . . . c_0 halved to 9.65 A. This point is of some importance since the 19.3 A period is characteristic of the fully hydrated phases in the autunite group, while the meta-I hydrates have a cell . . . with c_0 halved." The new data for meta-uranocircite invalidates this criterion for distinguishing the hydrates.

The new cell constants for meta-torbernite and meta-autunite agree closely with those given in Dana (1951). Beitema did not detect the doubled c value for meta-uranocircite in his analysis of the powder pattern of artificial material.

The space group in each case is *P4/nmm*. It is certain therefore, that our specimen of uranocircite is actually meta-uranocircite. The doubled c length is most likely due to the larger ionic radius of Ba as compared to Cu and Ca (Ba^{2+} 1.43, Cu^{+} 0.96, Ca^{2+} 1.06; Evans, 1948, p. 171).

The cell contents of meta-uranocircite were calculated using Winkler's analysis and the specific gravity 4.08, measured in this study. The calculated cell contents (Table 1) approach closely the ideal formula $2[BaO(UO_3)_2P_2O_5 \cdot 8H_2O]$ or $2[Ba(UO_2)_2(PO_4)_2 \cdot 8H_2O]$ which is the generally accepted formula for uranocircite (Dana, 1951, p. 987).

TABLE 1. META-URANOCIRCITE, ANALYSIS AND CELL CONTENTS

	I	II
BaO	15.08	2.0
UO_3	56.86	4.0
P_2O_5	15.06	2.1
H_2O	13.99	15.6
	100.99	

I. Falkenstein, Saxony; anal. Winkler (Weissbach, 1877 in Dana, 1892, p. 859). II. Unit cell contents.

As a check on the x-ray results obtained on natural meta-uranocircite, artificially prepared material was studied. A crystal of meta-autunite I from Autun, France which had been previously used for the determination of the cell constants of meta-autunite I was immersed in concentrated $BaCl_2$ solution at 100° C. for several hours and then used to obtain a zero-layer Weissenberg film about the *a*-axis. This film was identical with the one obtained from meta-uranocircite, Falkenstein, Saxony with the extra diffractions leading to a doubled *c* axis quite apparent. This crystal was found to be almost optically uniaxial with an index measured on the plates of 1.619 (as compared to 1.621, 1.622 measured on natural meta-uranocircite). Micro-chemical tests showed the presence of Ba, but no Ca.

A second specimen labelled uranocircite, this one from Madagascar (ROM M 15590) was found to show considerable variation in optical properties, ranging between those of meta-autunite and meta-uranocircite. At one end of the variation the plates have a low birefringence, very small $2V$ and faint twinning. The index in the plane of the plates is 1.607 and the extinction direction is approximately 45° to the twinning direction. These data agree closely with the data obtained from the Sosa meta-autunite used for the single crystal study and this identification was confirmed by a Weissenberg study which gave the lattice dimensions of meta-autunite: *a* 6.96, *c* 8.47 A.

At the other end of this variation in optics, the plates have a higher birefringence and larger optic angle. The optical sign is negative. Indices of $Y = 1.620$ and $Z = 1.622$ measured in the plane of the plates are those of meta-uranocircite. The identification was again confirmed with single crystal *x*-ray films.

Single crystal films of a plate with refractive index intermediate to those of the two types described above showed only a faint indication of the doubled *c* length of meta-uranocircite. These observations suggest that an isomorphous series exists between meta-autunite and meta-uranocircite and that the Madagascar specimen contains several representatives of this series.

Material in moist atmosphere

It was decided to attempt the formation of a higher hydrate of Ba corresponding in structure to fully hydrated autunite. For comparison meta-autunite was first converted to autunite by immersion in cold water for several hours. It was observed that the newly-formed material had a minimum refractive index of 1.575 in the plane of the plates (Dana, 1951, p. 985 gives 1.575 and 1.578 for natural autunite) which increased rapidly during the oil immersion tests. Weissenberg films obtained from a cleavage flake indicated a tetragonal cell with dimensions which compare well with those determined by Beintema on natural autunite:

	a	*c*	*Space Group*
Nuffield & Milne	6.98 A	20.70 A	*I4/mmm*
Beintema	7.00	20.67	*I4/mmm*

Attempts to form torbernite by the same method were unsuccessful. This is the experience of other workers (Dana, 1951, p. 983).

Cleavage fragments of natural meta-uranocircite were immersed in cold water (between 0 and 5° C.) for 24 hours. When placed in immersion oils the optical properties of this hydrated material changed rapidly, approaching those of meta-uranocircite. This suggested that the compound is stable only in a moist atmosphere. A cleavage fragment of this hydrate was used to obtain Weissenberg films with *a*[100] as the rotation axis, a moist atmosphere being maintained in the camera to prevent loss of water and a return to the meta-uranocircite structure. The films are remarkably similar to those obtained from meta-uranocircite. They indicate that the lattice remains primitive (space group $P4_22$) unlike the inversion from meta-autunite to autunite; the length of the *a* axis is unchanged at 6.97 A while the *c* length is increased from 16.90 to 17.57 A. It may be assumed that no shift of the U-P-O sheets occurred during the hydration; the sheets have merely been more widely separated by the addition of water. The compound is not isostructural with autunite. Beintema's dehydration experiments suggest that the new hydrate has ten molecules of H_2O. The cell contents are probably $2[Ba(UO_2)_2(PO_4)_2 \cdot 10H_2O]$. It is unlikely that it exists in nature.

Table 2. *X*-ray Powder Data for Meta-uranocircite
Tetragonal, *P4/nmm; a* 6.96, *c* 16.90 A

I	*d* meas.	*d* calc.	*hkl*	I	*d* meas.	*d* calc.	*hkl*	I	*d* meas.
7	8.19	8.44	002	4	2.59	2.61	016	3	1.924
6	5.37	5.37	012	½	2.41	2.42	025	½	1.883
3	4.90	4.92	110	1	2.35	2.36	222	3	1.796
6	4.21	4.22	004	2	2.18	2.20	130	3	1.741
10	3.58	3.61	014			2.18	026	½	1.676
2	3.39	3.41	021	1	2.12	2.12	132	5	1.589
5	3.21	3.22	022			2.12	224	1	1.559
3	2.91	2.93	122	7	2.08	2.08	126	5	1.518
½	2.67	2.69	024	4	2.01	2.01	018		

Ni filtered Cu radiation; $\lambda = 1.54050$ A.

X-ray powder data for this compound and for naturally-occurring meta-uranocircite are given in Tables 2 and 3.

TABLE 3. *X*-RAY POWDER DATA FOR LABORATORY-HYDRATED META-URANOCIRCITE
Tetragonal, $P4_22$; a 6.96, c 17.57 A

	d				*d*				*d*
I	meas.	calc.	*hkl*	I	meas.	calc.	*hkl*	I	meas.
7	8.42	8.78	002	5	2.69	2.73	024	1	1.928
1	6.27	6.47	011	1	2.52	2.54	124	$\frac{1}{2}$	1.809
7	5.30	5.46	012	1	2.43	2.46	220	1	1.754
2	4.79	4.93	110	2	2.35	2.37	222	$\frac{1}{2}$	1.723
5	4.25	4.30	112	7	2.17	2.18	131	1	1.690
10	3.65	3.72	014	7	2.12	2.15	224	3	1.646
4	3.41	3.42	021	$\frac{1}{2}$	2.07	2.09	018	1	1.606
7	3.18	3.24	022	1	2.03	—	—	4	1.550
4	2.90	2.94	122	$\frac{1}{2}$	1.992	—	—	1	1.522

Ni filtered Cu radiation; $\lambda = 1.54050$ A.

Further observations

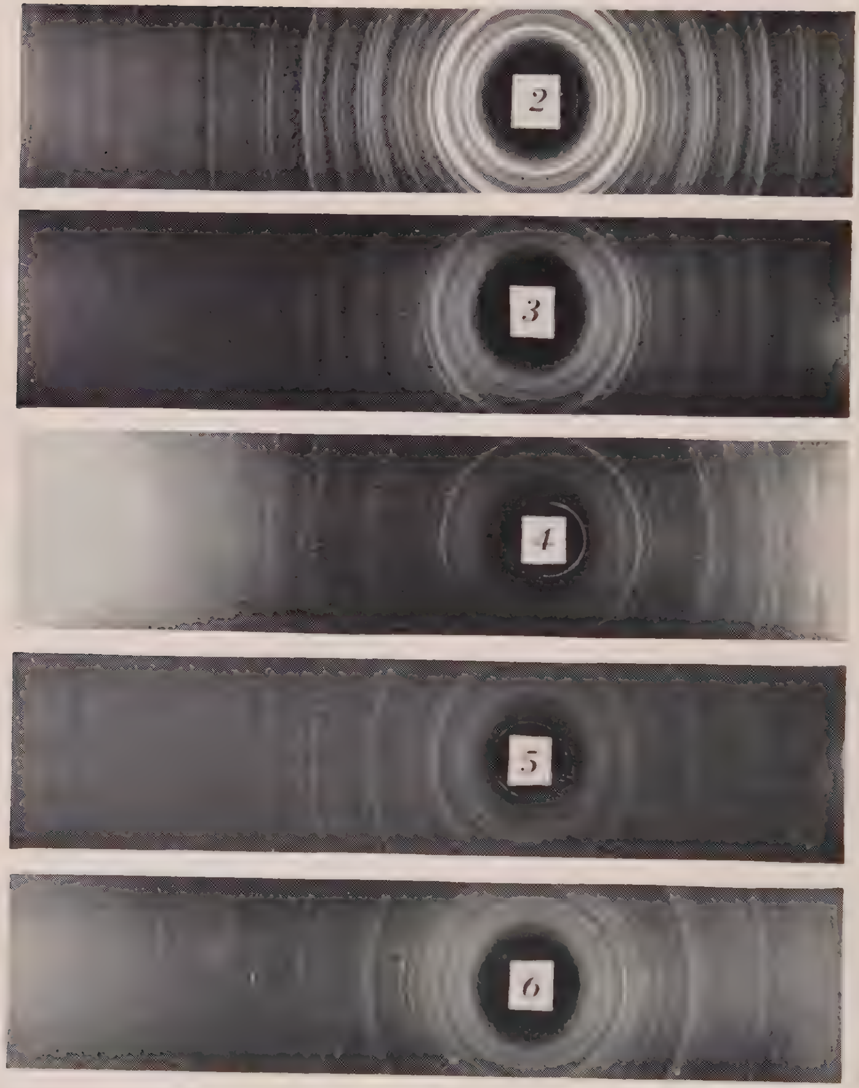
An interesting feature of the single crystal data which are available for the meta-phosphates is that the c dimension increases with decreasing ionic size of the cation:

Meta-uranocircite	$Ba(UO_2)_2(PO_4)_2 \cdot nH_2O$	$c = 8.45 \times 2$ A
Meta-autunite	$Ca(UO_2)_2(PO_4)_2 \cdot nH_2O$	8.47
Meta-torbernite	$Cu(UO_2)_2(PO_4)_2 \cdot nH_2O$	8.64

Ionic radii for C. N. 6 (Evans, 1948): Ba^{2+} 1.43, Ca^{2+} 1.06, Cu^{+} 0.96 (the ionic radius of Cu^{2+} which applies here and elsewhere in this paper, was not available), O^{2-} 1.32.

Where a disparity in radius between cation and anion occurs in ionic structures, coordination between these ions may be effected by water molecules. According to Evans (1948): "In many hydrates the function of water is simply to coordinate the cations and thereby effectively surround them with a neutral shell which increases their radius and enables their charge to be distributed over a greater number of anions." Hence there is a possibility of a small, highly polarizing cation having a large effective radius when coordinated by water molecules. Evidently in such hydrates the coordinated water molecules play an essential part in determining the stability of the structure as a whole and when removed result in the breakdown of the structure. This is in contrast to structural or zeolitic water which adds little to the stability of a structure and which may be removed without change to the structure. Compounds containing both coordinated and structural water are known.

The c periods of the meta-phosphates and the ionic radii of the cations suggest that the amount of coordinated water increases from the Ba mem-



FIGS. 2 to 6. *X*-ray powder patterns; Cu/Ni radiation; camera radius 90/π mm.; full size contact prints: 2—Meta-torbernite, Cornwall, England; 3—Meta-autunite, Sosa, Erzgebirge, Saxony; 4—Meta-uranocircite, Falkenstein, Saxony; 5—Autunite (artificial), prepared from meta-autunite, Autun, France; 6—hydrated meta-uranocircite, Falkenstein, Saxony; probable composition $Ba(UO_2)_2(PO_4)_2 \cdot 10H_2O$

ber to a maximum in the Cu member. To test this, crystals of the three minerals were heated and their structures re-examined. A crystal of meta-torbernite from Cornwall, after heating at 110° C. for 24 hours gave single crystal films which indicated that the structure had collapsed forming a new cell, orthorhombic in symmetry and with dimensions *a* 6.57, *b* 6.95, *c* 6.75 A (as compared to the original tetragonal cell with *a* 6.96, *c* 8.64 A). A cleavage flake of meta-autunite from Autun, after heating for 24 hours at 130° C. gave single crystal films with rather diffuse diffraction spots. However it was readily deduced that the original tetragonal cell with *a* 6.96, *c* 8.47 A had shrunk to a tetragonal cell with identical *a* dimensions but with *c* 8.14 A.[1] A sample of meta-uranocircite heated to 105° C. for 40 hours and another heated to 500° C. confirmed the findings of Beintema that the meta-uranocircite structure is not destroyed under these conditions. It may therefore be assumed that the water in meta-uranocircite is largely zeolitic; that it is partly coordinated water in meta-autunite and largely coordinated in meta-torbernite. The optical data recorded above for the three compounds support this assumption. Our two meta-uranocircite specimens show pronounced birefringence in the plane of the plates and a measurable 2V angle. The meta-autunite specimens show faint birefringence but with the indices in the plane of the plates sensibly the same. The angle 2V is very small. The meta-torbernite specimen which was studied has uniaxial optical properties. However, the *x*-ray photographs show no departure from tetragonal symmetry in each of the three cases. Neither the presence of twinning in meta-uranocircite nor a variation in the extinction direction in meta-autunite can be detected by *x*-ray diffraction. It may be fairly assumed that these optical effects in meta-uranocircite and meta-autunite are anomalous which can be attributed only to water molecules which are relatively free to move within the structure, that is zeolitic rather than coordinated water. Because the anomalous effects are most evident in meta-uranocircite and absent in meta-torbernite, one is again led to the conclusion that the water in meta-uranocircite is largely zeolitic, decreasing in meta-autunite, and is largely coordinated in meta-torbernite. The above observations indicate further that the members of the meta-torbernite group are not strictly isostructural.

The fully hydrated phosphates in contrast to the meta-phosphates show an increase in the *c* period with increase in the size of the cation present:

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[1] Beintema deduced an orthorhombic cell with dimensions *a* 6.46, *b* 6.98, *c* 8.67 A from powder photographs of material heated to 70° C.

		c	Ionic Radii C.N. 6 Evans (1948)	
Sabugalite[a]	$HAl(UO_2)_2(PO_4)_2 \cdot nH_2O$	19.3	Al^{3+}	0.57
Saleeite[b]	$Mg(UO_2)_2(PO_4)_2 \cdot nH_2O$	19.84	Mg^{2+}	0.78
Torbernite[c]	$Cu(UO_2)_2(PO_4)_2 \cdot nH_2O$	20.54	Cu^{+}	0.96
Autunite	$Ca(UO_2)_2(PO_4)_2 \cdot nH_2O$	20.70	Ca^{2+}	1.06

[a] Frondel 1951a, p. 674.

[b] Frondel 1951b, p. 681.

[c] Dana 1951, p. 982; converted to A units.

Beintema's analysis of the structure of autunite did not yield a unique position for the Ca atoms. Of the two possible positions between the sheets, he arbitrarily chose the large cavities (000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$) in preference to the (*b*) positions (00$\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}$0). The cavities provide ample space for even the largest of the cations. If the cations are not coordinated by water molecules, their size can in these positions have no effect upon the distance between adjoining sheets. On the other hand, if the cations are coordinated by water, highly charged, small cations such as Al might be expected to form the larger cells. However in sabugalite, the sheets are distinctly closer together than they are in autunite. In contrast, the (*b*) positions (see Fig. 1b) are sufficiently small to ensure that the distance between adjoining sheets will be sensitive to the ionic size of the cation occupying them. Since the single crystal data show a dependence of c period upon cation radius, it seems certain that the (*b*) rather than the (*a*) positions are occupied by the cations.[1]

This view of the structure of autunite is supported by the data of Table 4 which shows the propensity of various ions to form compounds of the meta-phase or the fully hydrated-phase for both phosphates and arsenates. The data of the table indicate that under like conditions of temperature and humidity, the stability of the fully hydrated structure increases with decrease in the ionic radius of the cation. Uranospinite (Mrose, 1951) is not an anomaly; Beintema has pointed out that there are not enough identity positions in the fully hydrated structure to effect valence compensation by a monovalent ion. Uranocircite has the largest cation; it is found in nature with the meta-structure and cannot be transformed to the fully hydrated structure in the laboratory. Zeunerite (J. W. Frondel, 1951) occurs in nature as the meta-structure. Natural material cannot be converted to the fully hydrated structure although synthetic zeunerite may be precipitated from solution in the laboratory. Torbernite and autunite are rarely found as fully hydrated structures, and then presumably in damp climates. Specimens of these two species collected and housed in North America are invaribaly of the meta-type. Autunite can be formed from meta-autunite; meta-torbernite cannot be prepared. Novacekite (Frondel, 1951b), saleeite and sabugalite exist in American collections as fully hydrated structures. The obvious explanation for these data is that as the radius of the cation which binds the sheets in the fully hydrated structure increases (see Fig. 1), the structure becomes more precarious. The radii of Cu^{2+} and Ca^{2+} apparently represent the transition zone when the structure becomes meta-stable and the tendency is for the sheets to slide over one another in order to form the more stable (for this ionic radius) meta-structure. The radius of Ba^{2+} may be of such a size as to make a stable, fully hydrated phase impossible.

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[1] It is interesting to note that for this arrangement of atoms, the U^{6+} ion may be calculated to have a maximum radius of 0.6 A from the data given by Beintema for the structure of autunite.

Table 4. Relation between Composition and Structure

	A	*X*	Occurrence in Nature
Sabugalite	HAl	P	As fully hydrated structure only
Saleeite	Mg	P	
Novacekite	Mg	As	
Autunite	Ca	P	Rarely as fully hydrated structure; usually as meta-structure
Torbernite	Cu	P	
Zeunerite	Cu	As	As meta-structure only
Uranocircite	Ba	P	
Uranospinite	H	As	

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THE STRUCTURE OF PUCHERITE, $BiVO_4$

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ABSTRACT

The structure of pucherite, $BiVO_4$, ($a=5.33_2$A, $b=5.06_0$A, $c=12.02_0$A, $Z=4$, space group *Pnca*) has been analysed by Patterson projections and refined by Fourier and (F_0-F_c) syntheses. Atomic coordinates and interatomic distances are given. A preliminary structure reported earlier has been confirmed except for the positions of eight O in two sets of special positions that are now shown to be in general positions. An interesting relationship between the BiOCl structure and those of $BiVO_4$ and tetragonal $BiAsO_4$ is demonstrated.

INTRODUCTION

In any general study of the role of vanadium in the structures of the vanadium minerals (Barnes & Qurashi, 1952), mixed oxides form a logical bridge between the oxides of vanadium, such as V_2O_5 (Ketelaar, 1936; Byström, Wilhelmi & Brotzen, 1950), and the more complex vanadates. It is, therefore, of interest to obtain reasonably accurate interatomic distances in a structure such as that of pucherite, $BiVO_4$. A preliminary structure for this mineral has been proposed (Quarashi & Barnes, 1952). In the present paper details of the analysis of Patterson projections are given and the refinement of the structure by Fourier and difference syntheses is described.

INTENSITY DATA

The intensity data for the three principal zones were collected by means of Buerger precession photographs using Mo K_α radiation ($\lambda=0.7107$A) and $\bar{\mu}=25°$. The crystal fragments were almost cubical in shape with linear dimensions of the order of 50 to 80 microns. Even for crystals as small as these, absorption corrections are significant; they were determined by standard graphical methods. Intensities were estimated visually from series of graded exposures (i.e., multiple exposures, not multiple *film* exposures as stated previously), using internal standards of intensity, since multiple film technique is not applicable to precession photographs. A later estimation of the intensities showed a standard deviation of about 15% compared with the earlier one. Taking this figure as a measure of the probable accuracy of the observations, the structure factors obtained from them should be accurate to about 8%. Lorentz-polarization factors were determined graphically with the aid of formulae given by Evans, Tilden & Adams (1949) and by Waser (1951). The observed intensities were placed on an absolute scale by the method of Wilson (1942; also, see Harker, 1948), wherein a graph of log $(\sum_j f_j^2/I_{obs.})$ is plotted against $(\sin\theta/\lambda)^2$ and the scale factor is obtained by finding the intercept at $(\sin\theta\ \lambda)^2=0$. This procedure gives correct scaling to within about 10%.

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PATTERSON PROJECTIONS

Patterson projections for the *h*0*l* and 0*kl* zones are shown in Fig. 1. For these syntheses the intensities were scaled only approximately, and the scale for the 0*kl* projection is about 20% lower than that for the *h*0*l*. A converging factor of $\exp(-4(\sin\theta/\lambda)^2)$ was applied because the observed intensities are appreciable even for reflections of the highest indices. From the fact that the height of a Patterson peak is approximately proportional to the product of the scattering factors of the two atoms giving rise to the peak, the peak heights for the various vectors can be deduced. Thus, taking the average height of the origin peaks (135 and 110) of the two projections (Fig. 1) as 122, the following estimates of the

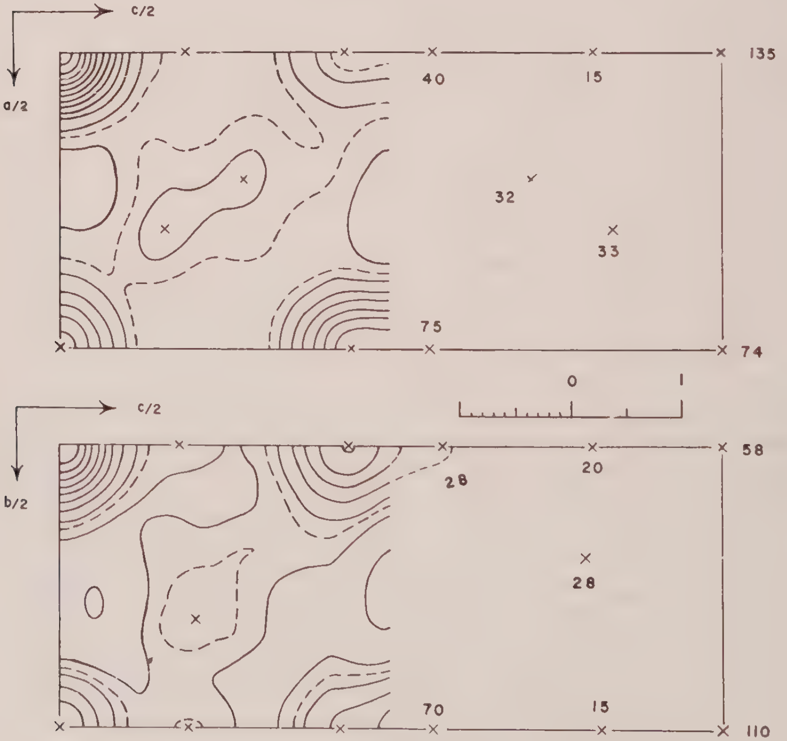

FIG. 1. Patterson projections of pucherite (scale in A).

peak heights of unit weight are obtained: Bi-Bi, 28; Bi-V, 7.0; Bi-O, 2.8; V-V, 1.7; V-O, 0.6; O-O, 0.2. It is clear that peaks due to V-V, V-O, and O-O will have almost negligible heights compared with the others and are unlikely to show up clearly on the Patterson maps. Analysis of the Patterson projections, therefore, must be confined largely to the identification of the peaks due to Bi-Bi, Bi-V, and Bi-O.

Retaining the same orientation for pucherite as selected previously (Qurashi & Barnes, 1952) to conform to the axial lengths of de Jong and de Lange (1936), $b<a<c$, the coordinates of the equivalent positions in the (centro-symmetrical) space group *Pnca* ($D_{2h}{}^{14}$) are

(*a*) $000;\ \frac{1}{2}00;\ 0\frac{1}{2}\frac{1}{2};\ \frac{1}{2}\frac{1}{2}\frac{1}{2},$
(*b*) $00\frac{1}{2};\ \frac{1}{2}0\frac{1}{2};\ 0\frac{1}{2}0;\ \frac{1}{2}\frac{1}{2}0,$
(*c*) $\frac{1}{4}0z;\ \frac{3}{4}0\bar{z};\ \frac{1}{4}\frac{1}{2},\ \frac{1}{2}+z;\ \frac{3}{4}\frac{1}{2},\ \frac{1}{2}-z,$
(*d*) $xyz;\ \frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{1}{2}-z;\ \bar{x},\ \frac{1}{2}+y,\ \frac{1}{2}-z;\ \frac{1}{2}-x,\ \bar{y},\ z;$
and these with changed signs.

Since there are only 4 Bi per unit cell, they must occupy one of the sets of special positions (*a*), (*b*), or (*c*). Now there are peaks in the Patterson maps (Fig. 1) at ($\frac{1}{2}$, —, 0) and (—, $\frac{1}{2}$, 0) with observed heights of 74 and 58, respectively. It is unlikely, however, that these arise from Bi atoms in positions (*a*) or (*b*) because such sites for Bi would result in a Patterson peak height of $4\times 28=112$, or more. (It will be shown later that they are, in fact, due largely to Bi-V vectors). The Bi atoms, therefore, must be in positions (*c*). This deduction is supported by the presence of Patterson peaks (Fig. 1) at ($\frac{1}{2}$, —, $\frac{13}{60}$) and (—, 0, $\frac{13}{60}$) which are the highest (75 and 70) observed. Thus a typical Bi-Bi peak is located at ($\frac{1}{2}$, 0, $\frac{13}{60}$). The coordinates of the Bi atoms, in special positions (*c*), therefore, are established as ($\frac{1}{4}$, 0, 0.108), etc., and the calculated height of a corresponding Bi-Bi Patterson peak is $2\times 28=56$.

Since the 4V also must be in positions (*a*), (*b*), or (*c*), Bi-V Patterson peaks must occur with x equal to 0, $\frac{1}{4}$, or $\frac{1}{2}$, and y equal to 0 or $\frac{1}{2}$. Therefore, the peaks previously examined at ($\frac{1}{2}$, —, 0) and (—, $\frac{1}{2}$, 0), of observed heights 74 and 58, together with those at (0, —, $\frac{13}{60}$) and (—, $\frac{1}{2}$, $\frac{13}{60}$), of observed heights 40 and 28 (see Fig. 1), can be identified as Bi-V. They constitute a set of the second highest peaks in the two Patterson projections.

From the presence of two Bi-V peaks having $z=\frac{13}{60}$ it follows that the V atoms must also be in special positions (*c*) but with coordinates ($\frac{1}{4}$, 0, $\frac{1}{2}-\frac{13}{60}$), etc. The calculated heights of corresponding Patterson peaks are $8\times 7.0=56$ at $z=0$ and $4\times 7.0=28$ at $z=\frac{13}{60}$. It may now be noted that the calculated values for the Bi-Bi Patterson peaks should be increased by about 6% since the V-V and Bi-Bi vectors coincide.

Finally the remaining Patterson peaks in Fig. 1 presumably must be

Bi-O since the heights of those due to V-V, V-O, and O-O, would certainly be less than 10.

As may be appreciated, the precise location of the 16 oxygen atoms in the unit cell is more difficult. The presence of Patterson peaks at x, $y \sim \frac{1}{4} \pm \frac{1}{30}$ shows that at least eight must be in general positions (d) with approximate coordinates $(-\frac{1}{30}, \frac{1}{4}+\frac{1}{30}, \frac{1}{4}-\frac{1}{30})$, etc., as given previously (Qurashi & Barnes, 1952, p. 424). The remaining eight O were placed originally in special positions (a) and (b) on the basis of the small Patterson peaks (observed heights, approximately 15) along x, $y=0, \frac{1}{2}$. Refinement of the structure has shown that this deduction is incorrect. Some indication of possible misinterpretation of these small peaks is given by the calculated value of 15 (against the observed 30) for the Patterson peaks along x, $y \sim \frac{1}{4} \pm \frac{1}{30}$ (after making allowance for V-O interactions and overlapping) if only eight O are placed in general positions. This, however, is not very conclusive due to the "background" usually present in Patterson maps.

FOURIER PROJECTIONS

The analysis of the Patterson projections fixes the positions of the bismuth and vanadium atoms with considerable certainty. Since the contribution of the oxygen atoms to the structure factor for any given reflection generally will be much less than that of the metal atoms, it should be possible to obtain the signs of most of the structure factors from the metal atom contributions alone.

The structure factor data are given in Table 1, where the values of F calculated for the metal atoms ($F_{c(m)}$) may be compared with the observed structure factors ($|F_0|$). In only one case, (017), is there any real doubt regarding the sign of any of the observed $h0l$ and $0kl$ reflections. (Fortunately $|F_0|$ for 017 is small so that it could be omitted from the preliminary Fourier synthesis without risk of serious error.) Using the signs so determined, the ac and bc Fourier projections were calculated, with a converging factor of $\exp(-3(\sin\theta/\lambda)^2)$, and are shown in Fig. 2. They are particularly interesting because all the oxygen atoms emerge quite clearly in two sets of eight-fold positions.

The observed Patterson peaks in Fig. 1, for which x, $y \sim \frac{1}{4}$, can now be assigned to Bi-O vectors, while those of height 15, along x, $y=0$ (Fig. 1), correspond to the small bulges in the Fourier maps (Fig. 2) near the bismuth atoms and probably are due to diffraction effects and cumulative observational errors.

While the Fourier projections of Fig. 2 show the four-fold coordination of oxygen atoms around the atoms of vanadium, they are consistent with two possible arrangements, one of which is nearly tetrahedral and the

Table 1. Structure Factor Data for $h0l$ and $0kl$ Zones ($|F_0|$, Observed; $F_{c(m)}$, Calculated for Metal Atoms Only; F_c, Calculated with Final Coordinates)

hkl	$F_{c(m)}$	$\|F_0\|$	F_c	*hkl*	$F_{c(m)}$	$\|F_0\|$	F_c
000	404	552	552	011	164	188	160
002	78	83	84	013	$\overline{88}$	59	$\overline{64}$
004	$\overline{298}$	242	$\overline{254}$	015	$\overline{174}$	188	$\overline{186}$
006	$\overline{166}$	126	$\overline{127}$	017	6	28	29
008	154	135	136	019	131	112	125
0.0.10	172	182	167	0.1.11	43	<35	26
0.0.12	$\overline{47}$	61	$\overline{69}$	0.1.13	$\overline{79}$	76	$\overline{72}$
0.0.14	$\overline{137}$	~ 190	$\overline{131}$	020	308	314	251
102	$\overline{202}$	190	$\overline{190}$	022	63	<50	35
104	$\overline{79}$	41	$\overline{56}$	024	$\overline{249}$	305	$\overline{273}$
106	136	145	161	026	$\overline{145}$	142	$\overline{149}$
108	110	90	96	028	137	147	140
1.0.10	$\overline{59}$	66	$\overline{77}$	0.2.10	156	146	140
1.0.12	$\overline{99}$	81	$\overline{79}$	0.2.12	$\overline{44}$	39	$\overline{40}$
200	$\overline{313}$	285	$\overline{234}$	031	123	113	118
202	$\overline{65}$	51	$\overline{60}$	033	$\overline{68}$	81	$\overline{98}$
204	252	290	273	035	$\overline{136}$	96	$\overline{114}$
206	147	145	153	037	5	<35	$\overline{2}$
208	$\overline{139}$	169	$\overline{162}$	039	108	91	105
2.0.10	$\overline{157}$	145	$\overline{135}$	0.3.11	37	24	31
2.0.12	44	40	39	040	207	207	198
302	158	192	173	042	43	59	66
304	63	44	51	044	$\overline{176}$	155	$\overline{159}$
306	$\overline{110}$	86	$\overline{91}$	046	$\overline{104}$	80	$\overline{92}$
308	$\overline{91}$	53	$\overline{60}$	048	103	100	110
3.0.10	51	63	72	0.4.10	123	100	98
3.0.12	88	80	80	051	85	72	83
400	215	228	227	053	$\overline{46}$	38	$\overline{38}$
402	44	<35	33	055	$\overline{95}$	69	$\overline{81}$
404	$\overline{181}$	170	$\overline{170}$	057	3	<35	10
406	$\overline{110}$	92	$\overline{89}$	060	135	130	122
408	108	94	96				
4.0.10	127	123	114				
502	$\overline{107}$	80	$\overline{89}$				
504	$\overline{44}$	<35	$\overline{31}$				
506	79	80	98				
508	69	52	58				
600	$\overline{144}$	136	$\overline{129}$				
602	$\overline{30}$	34	$\overline{33}$				
604	125	~ 93	112				

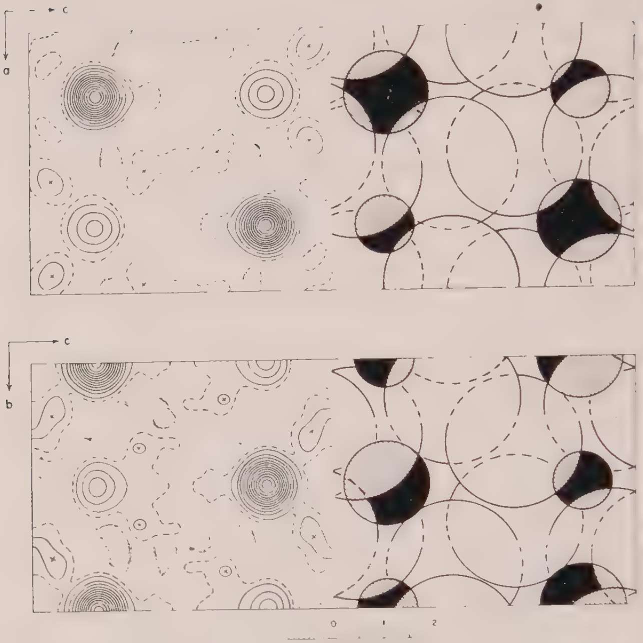

FIG. 2. Pucherite, BiVO$_4$, $h0l$ & $0kl$ projections (scale in A). Fourier maps on left; contours at intervals of $10e.A^{-2}$ with the $5e.A^{-2}$ line broken; zero contours dotted; approximate O positions indicated by crosses. Schematic structure on right; small solid circles, V; large solid circles, Bi; very large open circles, O; solid circles are hatched where overlaid by O.

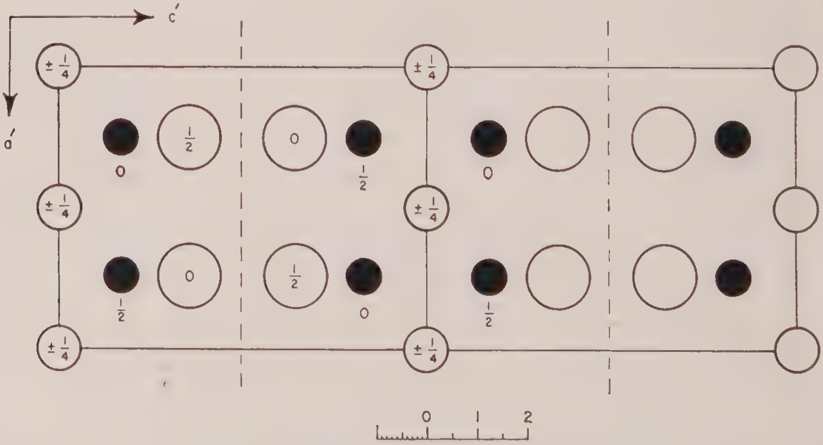

FIG. 3. BiOCl, $h'0l'$ projection (scale in A); solid circles, Bi; small open circles, O; large open circles, Cl.

other is nearly planar. Although the planar coordination can be rejected on spatial grounds and because it would require a shortest O-O distance of 2.06A, it is of interest to examine the *hk*0 zone for possible information. The zero level, *c* axis, precession photograph, therefore, is reproduced in Fig. 4 and it will be seen that all reflections with both *h* and *k* even are equally strong when allowance is made for Lorentz-polarization and scattering factors. While this is in agreement with the proposed structure, for which $F_{hk0} = 4f_{Bi} + 4f_V +$ (oxygen contributions), when *h* and *k* are both even, it is clearly not suitable for establishing the configuration of the oxygen atoms. Due to the *a* glide, the only other observable reflections in this zone have *h* even and *k* odd. In Table 2, the estimated structure factors ($|F_0|$) for these few reflections are compared with those calculated for a planar arrangement of the oxygen atoms ($F_{c(p)}$) and for a tetrahedral arrangement ($F_{c(t)}$), respectively; agreement with $|F_0|$ is better for the tetrahedral coordination. It is obvious, from the small values of F_0 for these reflections, that the corresponding spots will not be visible in the reproduction (Fig. 4).

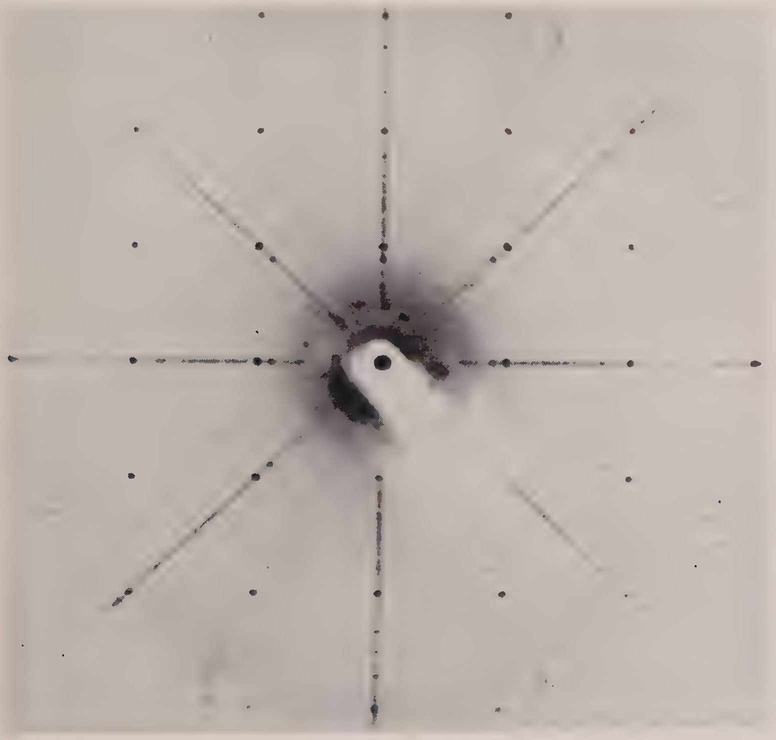

FIG. 4. Pucherite, *c* axis zero-level precession photograph; *b**, horizontal; *a**, vertical; (unfiltered Mo radiation).

Although the salient features of the pucherite structure are brought out reasonably well by the Fourier projections of Fig. 2, the oxygen contours and peak heights are not entirely satisfactory. This is largely the result of diffraction (i.e., series termination) effects and can be overcome by means of successive difference syntheses.

TABLE 2. STRUCTURE FACTORS FOR *hk0* ZONE; *h* EVEN, *k* ODD ($|F_0|$, OBSERVED; $F_{c(p)}$, CALCULATED FOR PLANAR OXYGENS; $F_{c(t)}$, CALCULATED FOR TETRAHEDRAL OXYGENS)

*hk*0	$F_{c(p)}$	$\|F_0\|$	$F_{c(t)}$
210	34	10	13
230	$\overline{10}$	16	$\overline{15}$
410	28	<20	9
430	$\overline{9}$	<20	$\overline{15}$

REFINEMENT BY DIFFERENCE SYNTHESES

Structure factors for all observable reflections were calculated using atomic positions obtained from the Fourier maps of Fig. 2. Atomic scattering factors were obtained from the *Internationale Tabellen* (1935). Since the state of ionization of the atoms is uncertain, estimates were made for $Bi^{+1.5}$, $V^{+2.5}$, O^{-1}. A temperature factor, $\exp(-B(\sin\theta/\lambda)^2)$ was employed to simulate experimental conditions. During refinement, values of B, obtained by plotting $|F_c|/|F_0|$ as functions of $(\sin\theta\ \lambda)^2$, altered from -1.0 to $-1.3A^2$. The final value corresponds to a thermal vibration of amplitude 0.13A. This is reasonable although much reliance cannot be placed on the absolute value of B.

Fourier syntheses were made using (F_0-F_c) in place of F_0 and the

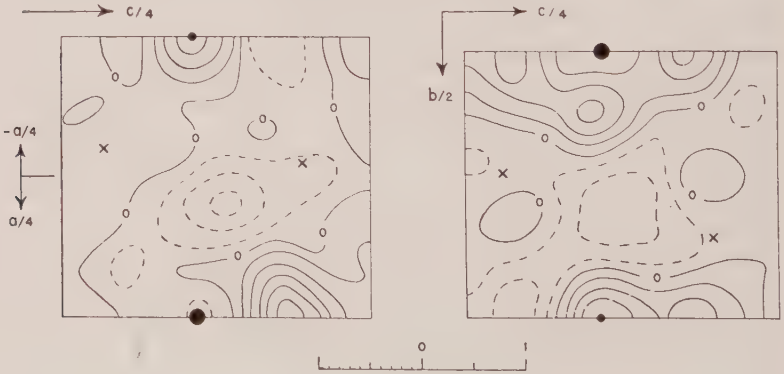

FIG. 5. Pucherite, $BiVO_4$, difference $(\rho_0-\rho_c)$ maps (scale in A); contours at intervals of $1e.A^{-2}$ with zero contour labelled and negative contours broken; small solid circles, V; larger solid circles, Bi; O positions indicated by crosses.

resulting difference projections were plotted. Cochran (1951) and others have described how shifts in atomic coordinates and other details are determined from such data. The final difference maps, obtained after three successive refinements, are shown in Fig. 5. The criterion for correctness of the coordinates used in the calculations is that the gradient should be zero at all atomic positions. This is fulfilled in the maps of Fig. 5, with the exception of one oxygen position in the *h*0*l* projection which requires a shift of -0.01A in the x coordinate.

It will be observed that ripples are prominent in the neighbourhood of the metal atoms. The peaks surrounding the bismuth atoms cannot be interpreted as due to any appreciable excess thermal vibration, nor can the large positive peak at the vanadium position be taken as indicating a smaller value of B in the temperature factor because the necessary reduction would make B negative for vanadium. Since the peak at the vanadium position appears in both difference projections (Fig. 5) it may be genuine, and not simply the result of cumulative errors. In this case it may conceivably be due to the poor approximation of the Thomas-Fermi scattering curves for a light atom such as vanadium.

The final atomic coordinates are collected in Table 3 together with standard deviation, $\sigma(u)$, for each. The latter were obtained by calculating the root-mean square gradient $\sqrt{\overline{(\partial D/\partial u)^2}}$, and using the formula $\sigma(u)=\sqrt{\overline{(\partial D/\partial u)^2}}/2p\rho(0)$ (*cf.*, Cochran, 1951, pp. 83, 89), where $D=(\rho_0-\rho_c)$ is the electron density in the difference map. It will be noticed in Table 3 that the scatter of the z coordinates about the mean values for the two projections is of the order of the corresponding estimated $\sigma(z)$ in the case of oxygen, but is considerably greater than $\sigma(z)$ in the case of

TABLE 3. ATOMIC COORDINATES (IN A) AND STANDARD DEVIATIONS
($a=5.33_2$A, $b=5.06_0$A, $c=12.02_0$A)

	x	y	z	z (mean)	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Bi	5.332/4	—	1.325	1.318	0	0	0.003
	—	0	1.311				
V	5.332/4	—	4.754	4.734	0	0	0.011
	—	0	4.715				
O_I	-0.28	—	0.42	0.38	0.04	0.05	0.03
	—	-1.16	0.34				
O_{II}	-0.16	—	2.32	2.35	0.04	0.05	0.03
	—	1.77	2.38				

the metal atoms. This is due in part to the fact that the (F_0-F_c) terms used in the final synthesis were weighted inversely as the probable errors in the estimations of $|F_0|$. This procedure gives the weaker reflections proportionately greater weight, and ultimately improves the accuracy of the oxygen parameters.

The standard deviations are lowest for the z coordinates because the final values were averaged over both projections.

Values of F_c, calculated with the coordinates of Table 3, will be found in Table 1. The reliability index, $R=\sum[|F_0|-|F_c|]\ \sum|F_c|$, is 0.10 for each zone. This compares favourably with the estimated error in F_0 of about 8%.

INTERATOMIC DISTANCES, AND DISCUSSION

The bonding of both kinds of metal atoms to their nearest oxygen atoms shows clearly in the Fourier maps (Fig. 2), but, whereas V atoms are bonded only to four O atoms, the Bi atoms have additional bonds to O atoms across $z=0$ and $z=\frac{1}{4}$. The interatomic distances are given in Table 4.

TABLE 4. INTERATOMIC DISTANCES (IN A)

V-O_I,	1.95 ± 0.07	Bi-O_I,	2.20 ± 0.06	O_I-O_I,	2.50, 2.78; 3.14, 3.45
V-O_{II},	1.76 ± 0.07	Bi-O_{II},	2.54 ± 0.07	O_{II}-O_{II},	2.86, 2.97; 2.80, 3.33
(V-O_I',	2.69 ± 0.07[1])	Bi-O_I',	2.31 ± 0.06[1]	O_I-O_{II},	3.04, 3.53; 2.80, 3.44
(V-O_{II}',	4.33 ± 0.07[2])	Bi-O_{II}',	2.73 ± 0.06[2]		

[1] Across $z=0,\ \frac{1}{2}$.

[2] Across $z=\pm\frac{1}{4}$; standard error of O-O distances, 0.1A.

It is of interest to note that the O_{II} atoms are bonded rather loosely to Bi but firmly to V, whereas the opposite is true of the O_I atoms. In fact, the Bi-O_{II}' distance (across $z=\pm\frac{1}{4}$) is so great (2.73A) as to suggest that most of the force across these planes must be due to O-O van der Waals interactions. This is apparent in the schematic structure comprising the right-hand side of Fig. 2, where radii approximately proportional to the ionic radii have been used for the circles representing the atoms.

The ratios of the univalent radii of the metal and oxygen atoms suggests six-fold coordination around vanadium. It is of interest to note that whereas such coordination occurs in tetragonal V_2O_4 (Wyckoff, 1948), it becomes intermediate between six-fold and four-fold in V_2O_5 (Ketelaar, 1936; Byström, Wilhelmi & Brotzen, 1950) and is clearly four-fold (tetrahedral) in pucherite, $BiVO_4$.

The univalent radius ratio favours either six-fold or eight-fold oxygen coordination around bismuth, depending on whether Bi^{+5} or Bi^{+3} is involved. If the long (2.73A) Bi-O$_{II}'$ bonds are included, the pucherite structure shows eight-fold coordination with two pairs of short bonds (2.20A, 2.31A) and two pairs of long bonds (2.54A, 2.73A). This arrangement is analogous to that in BiOCl, which has the PbFCl layer type structure, with $a=3.883$A, $c=7.348$A, space group *P*4/*nmm* (Wyckoff, 1948), and from which the structure of tetragonal BiAsO$_4$ (Mooney, 1948) and that of pucherite (BiVO$_4$) can be derived.

For direct comparison with the structure of pucherite, that of BiOCl is shown in projection in Fig. 3., where the diagonals of the unit cell of BiOCl have been taken as axes $a'=b'=5.49$A, and double the c axis as $c'=14.70$A. By replacing one-half the number of Bi atoms with As and all the Cl atoms with O, the structure of tetragonal BiAsO$_4$ can be obtained by small displacements of the O positions and by slightly larger displacements of the Cl positions (compare Fig. 3 with Fig. 1*b* of previous paper, Qurashi & Barnes, 1952, p. 425). In order to obtain the BiVO$_4$ structure, after substitution of one-half the number of Bi atoms with V and all the Cl atoms with O, a shift of alternate layers (separated by the broken lines in Fig. 3) through b′/2, parallel to the b' axis, is required.

The replacement of all the Cl atoms with O and of one-half the number of Bi atoms with V (or As) reduces the lengths of a', b', and especially c', observed in BiOCl. The decrease in the short Bi-O separation from 2.31A in BiOCl to an average of 2.26 ± 0.04A (for Bi-O$_I$ and Bi-O$_{II}$) in BiVO$_4$ may be significant. In addition, the average V-O separation in BiVO$_4$ is 1.86 ± 0.04A (for V-O$_I$ and V-O$_{II}$) which is about 0.10A greater than the normal V-O distance for tetrahedrally coordinated V^{+5} (*cf.* Ketelaar, 1936; Zachariasen, 1931). The oxygen coordination in pucherite, therefore, appears to be a compromise between configurations previously found for Bi^{+3} in BiOCl and for V^{+5} in V$_2$O$_5$. This suggests that the effective valence of Bi in BiVO$_4$ is somewhat greater than $+3$ while that of V is somewhat less than $+5$.

In BiOCl the predominant force holding the layers together across the planes $z=\pm\frac{1}{4}$ (see Fig. 3) is due to the Cl-Cl interactions since the Cl-Cl distance (3.48A) is much smaller than the radius sum while the Bi-Cl distance (3.49A) is significantly greater than the radius sum. It has already been pointed out that similar O-O interactions, rather than Bi-O forces, must be operative across the corresponding planes in pucherite (see Fig. 2). They are probably responsible for the perfect {001} cleavage.

In view of the interesting features of the pucherite structure, particularly the oxygen coordination around the metal ions, an attempt is being made to improve the accuracy of the metal-oxygen distances by a three-dimensional analysis using difference syntheses. It is hoped to report more accurate coordinates and interatomic distances in a subsequent note.

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PISANITE FROM FLIN FLON, MANITOBA[1]

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Abstract

An occurrence of blue zincian pisanite is described from Flin Flon, Manitoba. *X*-ray measurements give a monoclinic lattice, space group $P2_1/c$ with $a=14.12, b=6.54, c=10.81$A, $\beta=106°$. The unit cell contains 4 $[(Fe, Cu, Zn)SO_4\cdot 7H_2O]$ with Fe:Cu:Zn=100:80:3 and specific gravity 1.95 (calculated). *X*-ray measurements of a crystal of pure artificial $FeSO_4\cdot 7H_2O$ gave lattice dimensions $a=14.11$, $b=6.51$, $c=11.02$A, $\beta=105°15'$ with space group $P2_1/c$. The *x*-ray powder patterns of the two materials are almost identical.

During the summer of 1950, several specimens of a bright blue translucent mineral were sent to Professor Bruce Rose of Queen's University by Mr. Ken Rose, from the Cuprus mine about twelve miles east of Flin Flon, Manitoba The mineral occurs as a coarsely crystalline crust up to one quarter of an inch thick on iron, copper and zinc sulphide ores beneath the overburden and also in vugs within the ore and near the bedrock surface. The colour of the mineral is a somewhat lighter shade of blue than that of bluestone (chalcanthite $CuSO_4\cdot 5H_2O$).

A study of the material by *x*-ray methods soon identified it as a member of the melanterite group of minerals. The data obtained did not, however, agree completely with the published data collected in the recent works of reference (Winchell, 1951 and Dana, 1951). There are inconsistencies in the published data; Wyckoff (1951) quotes two sets of cell dimensions and concludes with the statement: "Evidently more work is needed." It is the purpose of this paper to present the new data and to compare it with that already published.

Crystallography

The mineral occurs as a crystalline crust without development of single crystals. The perfect (001) and poor (110) cleavaged (in the crystallographic setting used in Dana) are easily visible in crushed material and a cleavage fragment suitable for *x*-ray study is readily found.

A cleavage fragment was adjusted on the Buerger precession camera with the good cleavage perpendicular to the pinhole. An orientation precession film readily revealed the position of the symmetry plane. The fragment was then readjusted with the mono-clinic symmetry axis parallel to the dial axis of the instrument. Precession films were taken about the *a* axis (parallel to the good cleavage) and the *c* axis. The adjusted crystal was then transferred to the Weissenberg camera and rotation,

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[1] Referred to as cuprian melanterite in the abstract printed in the *Proceedings of the Royal Society of Canada, 1952, vol.* **46,** *p. 152.*

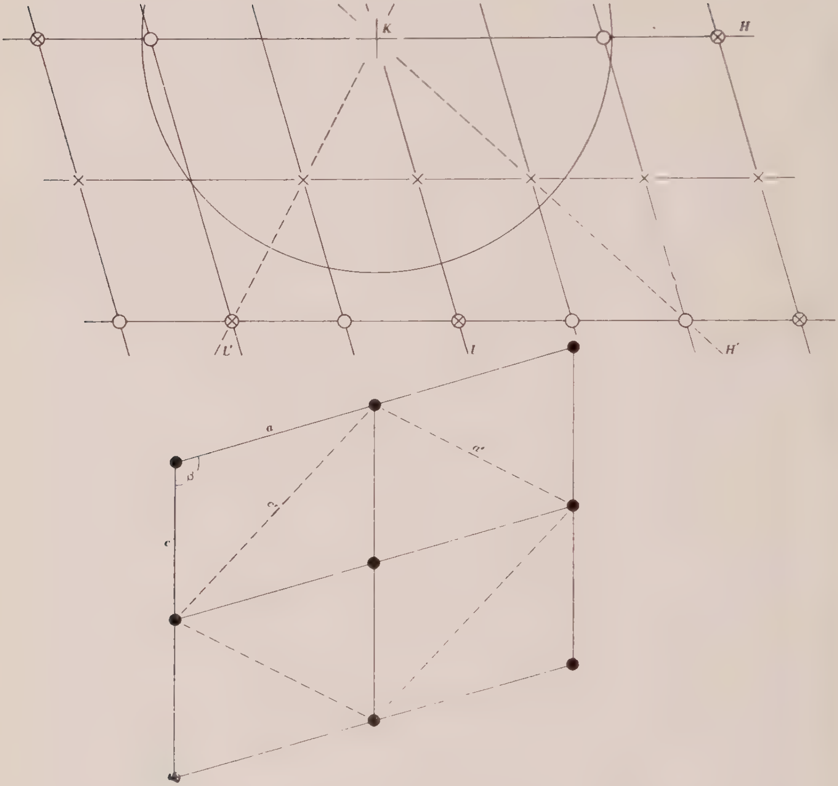

FIG. 1. Reciprocal lattice projection (top) and direct lattice (bottom) of melanterite and pisanite. The cell proposed in this paper is indicated by a, c, β and H, K, L. The B-centred cell of Ness is indicated by a', c', H', K' (the dashed lines). In the reciprocal lattice projection circles represent the observed $h0l$ diffractions and crosses the observed $h1l$ diffractions.

zero and first layer Weissenberg films were taken. Indexing of the precession films and the reciprocal lattice projections of the Weissenberg films (Figure 1) indicated a conventional cell of the monoclinic lattice with the following dimensions:

$$a = 14.12, \quad b = 6.54, \quad c = 10.81\text{A}, \quad \beta = 106°00'.$$

The observed diffractions conform to the following conditions: (hkl) all present, ($h0l$) present only for $l=2n$, ($0k0$) present only for $k=2n$. These criteria are characteristic of the space group $C_{2h}^5 - P2_1/c$. In this setting the cleavages are $(\bar{1}01)$ and (111) and the traditional morphological setting of Dana is related to the structural setting by the transformation formula: $10\bar{1}/010/101$.

A small crystal of chemically pure $FeSO_4 \cdot 7H_2O$ was mounted on the precession camera. The films indicated that the crystal lattice is very similar to that for the natural pisanite with space group $P2_1/c$ and lattice dimensions:

$$a = 14.11, \quad b = 6.51, \quad c = 11.02\text{A}, \quad \beta = 105°15'.$$

In Table 1, the lattice dimensions and axial ratios from the literature are listed for comparison with the data obtained here. The early data of Westenbrink (1926) have been accepted by Dana (1951) with the space group given more specifically. Ness (1940) obtained a shorter b axis and a different space group, the dimensions are given in the traditional morphological setting. Our data agree closely with those of Ness except for the Herman-Mauguin symbol for the space group. Wyckoff (1951) has given Ness' dimensions in a different setting.

TABLE 1. MELANTERITE AND PISANITE: CRYSTALLOGRAPHIC DATA

	a	b	c		Space Group	Z
Westernbrink (1927)	15.34	12.98	20.02[1]		C_{2h}^6	
Dana (1951)	—	—	—	[104°16′]	C_{2h}^6-F2/d	16
Ness (1940)	15.33	6.50	20.08[1]	[104 16]	C_{2h}^5-P2/c	8
Wyckoff (1951)	15.33	6.50	11.01[1]	118 21		4
Berry ($FeSO_4 \cdot 7H_2O$)	15.45	6.51	20.05A	104 30	$C_{2h}^5-B2_1/x$	8
	14.11	6.51	11.02A	105 15	$C_{2h}^5-P2_1/c$	4
	2.168	1	1.694	105 15		
Melanterite, Dana (1951)	2.1629	1	1.6969	105 30		
Keating & Berry (zincian pisanite)	15.24	6.54	20.01A	105 40	$C_{2h}^5-B2_1/x$	8
	14.12	6.54	10.81A	106 —	$C_{2h}^5-P2_1/c$	4
	2.159	1	1.653	106 —		
Pisanite (Dana, 1951)	2.1789	1	1.6876	106 48		

[1] Probably in kX units.

The morphological axial ratio accepted by Dana (1951), but with b halved, fits a B-centred cell of the structural lattice. However, there is no symbol for expressing the glide plane in this setting of the space group. The setting adopted here is that chosen by the usual conventions, with a and c the shortest translations in the symmetry plane and β least obtuse. It is a coincidence that the value for β in the two settings is very similar. Melanterite crystals are most commonly equant in habit and therefore the new setting proposed here would be just as convenient for the geometricl description of the crystals as the morphological setting hitherto accepted.

TABLE 2. MELANTERITE AND PISANITE: *X*-RAY POWDER DATA

Pisanite, Monoclinic, $P2_1/c$, $a=14.12$, $b=6.54$, $c=10.81$A, $\beta=106°$; $Z=4$

$FeSO_4 \cdot 7H_2O$			Pisanite, $(Fe, Cu, Zn)SO_4 \cdot 7H_2O$, Manitoba				
I	θ(Fe)	*d*(meas)	*I*	θ(Fe)	*d*(meas)	*hkl*	*d*(calc)
3	10.3°	5.42A	3	10.4°	5.37A	$\bar{1}11$	5.42A
10	11.5	4.86	10	11.5	4.86	111	4.88
						$\bar{2}02$	4.82
1	12.3	4.55	1	12.6	4.44	300	4.52
½	13.4	4.18	½	13.5	4.15	$\bar{1}12$	4.15
						012	4.07
1	14.0	4.00	1	14.0	4.00	211	4.01
						$\bar{3}02$	4.00
5	15.0	3.74	5	14.9	3.77	$\bar{3}11$	3.79
						310	3.72
½	15.7	3.58	½	15.4	3.65	112	3.68
						202	3.67
½	16.7	3.37	½	16.7	3.37	400	3.39
3	17.5	3.22	3	17.4	3.24	020	3.27
						311	3.27
			1	18.0	3.13	113	3.15
						021	3.12
1	18.2	3.10				$\bar{2}13$	3.09
			1	18.4	3.07	$\bar{1}21$	3.09
						013	3.06
1	18.9	2.99	1	18.8	3.01	302	3.02
						410	3.01
						121	2.99
1	19.5	2.90	½	19.5	2.90	$\bar{2}21$	2.93
						$\bar{3}13$	2.88
½	20.5	2.77	½	20.5	2.77	122	2.79
						022	2.77
3	20.8	2.73	3	21.0	2.70	411	2.72
						$\bar{2}22$	2.71
						500	2.71
						104	2.69
3	21.6	2.63	3	21.6	2.63	320	2.65
						122	2.64
						413	2.61

$FeSO_4 \cdot 7H_2O$			Pisanite, Manitoba			$FeSO_4 \cdot 7H_2O$			Pisanite, Manitoba		
I	θ(Fe)	*d*(meas)	I	θ(Fe)	*d*(meas)	I	θ(Fe)	*d*(meas)	I	θ(Fe)	*d*(meas)
1	23.0°	2.48A	—	—	—	½	33.6°	1.750A	1	33.5°	1.755A
½	23.8	2.40	—	—	—	½	34.8	1.697	1	34.7	1.701
2	24.8	2.31	2	24.7°	2.32A	—	—	—	½	35.6	1.664
½	28.0	2.06	1	27.7	2.08	½	36.7	1.621	½	36.4	1.632
—	—	—	1	28.4	2.04	—	—	—	½	37.6	1.588
2	28.9	2.00	2	29.0	1.998	½	38.5	1.556	1	38.2	1.566
2	29.6	1.961	2	29.6	1.961	½	39.3	1.529	—	—	—
½	30.4	1.914	1	30.9	1.886	1	40.2	1.501	1	40.0	1.507
3	31.4	1.859	2	31.6	1.849	½	41.4	1.465	1	45.8	1.351
—	—	—	½	32.6	1.798						

Composition and cell content

A partial analysis of the natural material gave the following atomic proportions of the metal ions present Fe:Cu:Zn = 100:80:3. A spectrographic analysis showed the presence of manganese in minor amount. This composition would lead to the name zincian pisanite as the most appropriate for this mineral. Although melanterite, $FeSO_4 \cdot 7H_2O$, pisanite $(Fe, Cu)SO_4 \cdot 7H_2O$ and boothite $CuSO_4 \cdot 7H_2O$ are isostructural there is no evidence of the existence of a continuous series between the copper and iron members in nature. The primitive cell of the structural lattice contains $4[(Fe, Cu, Zn)SO_4 \cdot 7H_2O]$.

The measured specific gravity 1.91 agrees fairly well with 1.95, calculated for the cell content $4[(Fe, Cu, Zn)SO_4 \cdot 7H_2O]$ with Fe:Cu:Zn = 100:80:3.

X-ray powder pattern

The powder patterns with FeKα-radiation are very similar for pisanite and artificial melanterite. The estimated intensities, (I) and measured spacings (d) are given in Table 2 for both materials together with the indices and calculated interplaner spacings for pisanite. This pattern is diagnostic of the melanterite group but the differences between the two patterns are not sufficiently significant to distinguish between melanterite and pisanite by the *x*-ray powder method.

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MINERALOGY OF THE YELLOWKNIFE BAY AREA, N. W. T.[1]

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ABSTRACT

The gold ores of the Yellowknife Bay area represent a type quite different from those found elsewhere in the Precambrian Shield of Canada, if not in all other parts of the world. They represent a close association of gold with the element antimony, with a virtually complete absence of the element tellurium.

From a study of polished sections of these ores, the author has arrived at some conclusions as to their chemical nature and their manner of formation.

The formation of the ores is believed to have taken place during several distinct periods by filling of zones of dilation accompanied by some metasomatic replacement. Each period was marked by the introduction of an ore-forming fluid of a composition dissimilar to those introduced during other periods. The emplacement of these fluids is believed to have been effected by successive dilations of the rocks in response to periodic deformations.

The first solution producing metallic mineralization, is believed to have been rich in Fe, As and S. A solution rich in S, Cu, Zn possibly Fe and minor Sn is considered to have produced the mineralization of the second period, whereas that of the third and last period

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[1] Part of a thesis submitted to fulfill requirements for the degree of Master of Arts, Queen's University, 1952.

is believed to have been effected by an antimony-rich solution containing S, Au, Ag and Pb. Many of the elements contained in minerals formed during the last two periods, are believed to have been derived from older minerals which have been replaced. Gold appears to have been deposited principally within the last period of mineralization, in close association with a suite of antimony-rich sulphosalts. Visible gold is present in greatest amounts where sulphosalts are most abundant.

In all, 119 polished section of ores from eight gold properties in the Yellowknife Bay area, were studied. The metallic minerals identified include three native elements, 12 sulphides, one antimonide, 10 sulphosalts and one oxide. This extensive array of minerals is composed of relatively few chemical elements: Au, Ag, Fe, Cu, Zn, Pb, Sn, Sb, As and S.

Aurostibite, a relatively new mineral, is described and its economic importance is discussed. The importance of *x*-ray powder identifications in studies of complex ores, is noted.

INTRODUCTION

The summer of 1950 was spent by the writer on a reconnaissance party of the Geological Survey of Canada, operating out of Yellowknife, N.W.T. In June of that year, the author was asked by Mr. R. W. Boyle, a graduate student at the University of Toronto, to undertake a study of the mineralogy of the ores from the mines of the Yellowknife Bay area, as part of a general research project involving study of the structural geology, the wall rock alteration associated with the shear zones, and the temperatures of deposition of the pyrite and quarts.

A previous study of the Yellowknife ores by Ridland (1941), had indicated the presence of an astonishing variety of minerals, but it was felt that this required confirmation by more precise methods of mineral identification.[1]

During the summer of 1950, a suite of samples was collected by Mr. Boyle for study by the author. This suite included samples of ore from the Giant Yellowknife, Con, Rycon, Negus, Akaitcho, Lynx and Captain properties. Polished sections of these samples were prepared at Queen's University. Another suite of polished sections was suppled by Dr. A. W. Jolliffe, and included specimens from the Giant Yellowknife, Con, Rycon, Negus and Ptarmigan properties; some of these specimens comprised part of the suite that had been studied by Dr. Ridland in 1940. These two suites were studied under a reflecting microscope. Because of the fine-grained intergrowth of the minerals, and the fact that many of the minerals observed had very similar optical and physical properties, considerable use was made of *x*-ray powder diffraction methods in their identification.

[1] Minerals reported by Ridland which have not been identified in the present work, are: the sulpharsenides (jordanite, guitermanite and lengenbachite) and the tellurides (nagyagite, sylvanite, calaverite, altaite and rickardite); the presence of tantalite, leucopyrite and cobaltite is regarded as questionable. The author examined polished sections in which Ridland had identified the above minerals, and identified all minerals in them by *x*-ray powder diffraction methods.

ACKNOWLEDGMENTS

The author acknowledges the assistance of Dr. A. W. Jolliffe whose supervision of this work and helpful suggestions, proved invaluable. To Dr. L. G. Berry, the writer is extremely grateful for the willing assistance offered in consultations on the crystallographic properties of the minerals.

The writer wishes to thank the Consolidated Mining and Smelting Company, Giant Yellowknife Gold Mines, Negus Gold Mines and Akaitcho Gold Mines, for permission to use ore spceimens from their properties, and for assistance in the collection of these samples. The author is also greatly indebted to Mr. R. W. Boyle, who collected most of the specimens used in this study. Acknowledgement is made to Dr. A. R. Graham of the Department of Mines and Technical Surveys, Ottawa, who willingly contributed information and data on the mineral aurostibite.

The author would like to thank Dr. E. Sampson for critically reading the manuscript, and for offering a number of useful suggestions as to the manner of presentation of the material.

GENERAL GEOLOGY

West of Yellowknife Bay, lava flows and interbanded fragmental rocks of the Yellowknife Group of Precambrian age, strike northeasterly and dip vertically or steeply southeastwards, with progressively younger members from northwest to southeast. They are intruded by many sills and dikes of altered diorite and gabbro, and by later unaltered diabase dikes. The whole belt is much disrupted by faults of two types: (a) early pre-diabase faults and (b) late post-diabase faults.

Most of the early faults are of the shear-zone type, along which chlorite schist or chlorite-sericite schist is developed across widths ranging from a few inches to several hundred feet. The post-diabase faults, on the other hand, are clean-cut, narrow fissures. The rock along them is brecciated, and a clay-like gouge may be present, but no schist has been formed.

The gold deposits of the area occur along the early shear-zone faults. They may be divided into two closely related types: (1) well-defined quartz veins introduced along narrow shear zones such as occur on the Rycon property, and (2) large lenticular masses of highly mineralized sericite schist and vein quartz that occur along shear zones, or systems of shear zones, up to several hundred feet wide. Included in the latter type are the Campbell Shear on the Negus property, and the large orebodies along the Con and Giant shear-zone systems.

For more detailed descriptions of the geology of this area, the reader is referred to works by Jolliffe (1942, 1946) and Henderson & Brown (1950).

MINERALOGY—GENERAL CONSIDERATIONS

The mineralogy of the Yellowknife ores is very complex. This complexity is due to a number of factors: the variety of minerals present, the similar optical and physical properties of many of these, and the fine texture and intimate intergrowths.

At first sight in the field, the vein material appears to be nearly barren of metallic minerals. On closer examination, these minerals are found to occur in small clusters or nests, in fine seams or veins, and in disseminated grains throughout the vein quartz and intermixed carbonates.

Because of the aforementioned complexity of the mineralogy, *x*-ray diffraction methods were extensively employed in the identification of the minerals. It was found that not only could identifications be made of mineral particles which were much too small for investigation by etch reactions and microchemical methods, but also that these identifications were of a very positive nature, since each mineral produced a distinctive powder pattern. Hence a true picture of the mineralogy of ores of this nature, can be obtained with certainty, only by employing such methods.

The following mineralogical description and discussion is based on a study of 72 polished sections made from the suite of samples collected by Mr. Boyle, and of 47 polished sections, supplied by Dr. Jolliffe, which had been prepared at the Mines Branch Laboratories, Ottawa. Of these 47 polished sections, 33 were part of a suite studied by Ridland (1941) in connection with his doctorate thesis, at Princeton University, from 1938 to 1940.

Considerable differences exist between the mineral identifications made by Ridland and those made by the author. These discrepancies are attributed to the differences in identification techniques employed. It is the author's opinion that, although Ridland's work was of a very careful and thorough nature, he was seriously handicapped in that his identifications were based on etch reactions and microchemical tests, rather than on the more precise *x*-ray diffraction methods.

OCCURRENCE AND DISTRIBUTION OF MINERALS

The following minerals were identified by *x*-ray powder diffraction methods:

1. Native Elements:	
Gold	Au
Lead	Pb
Antimony	Ab
2. Sulphides:	
Pyrite	FeS_2
Marcasite	FeS_2
Pyrrhotite	$Fe_{1-x}S$

Arsenopyrite	$FeAsS$
Gudmundite	$FeSbS$
Sphalerite	ZnS
Chalcopyrite	$CuFeS_2$
Stannite (zincian)	$Cu_2(Zn, Fe)SnS_4$
Galena	PbS
Stibnite	Sb_2S_3
3. Antimonide	
Aurostibite	$AuSb_2$
4. Sulphosalts	
Zinkenite	$Pb_6Sb_{14}S_{27}$
Semseyite	$Pb_9Sb_8S_{21}$
Boulangerite	$Pb_5Sb_4S_{11}$
Meneghinite	$Pb_{13}Sb_7S_{28}$
Berthierite	$FeSb_2S_4$
Chalcostibite	$CuSbS_2$
Jamesonite	$Pb_4FeSb_6S_{14}$
"Mineral Q"	Fe, Cu, Sb sulphide (minor Pb, Ag)
Vournonite	$PbCuSbS_3$
Tetrahedrite	$(Cu, Fe)_{12}(Sb, As)_4S_{13}$
5. Oxide	
Cassiterite	SnO_2

Besides the minerals listed above, chalcocite and covellite were noted in polished sections in minor amounts and were readily identified on the basis of their distinctive optical properties. In hand specimens taken from weathered outcrops, the following secondary minerals were also noted: limonite, malachite and azurite.

The ores from the properties in the Yellowknife Bay area are, in general, of one mineralogical type. That is, the suite of minerals that occurs in the ores is consistent throughout. There are, however, some differences in the relative amounts of these minerals, in specimens from different deposits within the area.

On a quantitative basis, the general type may be subdivided into: ores in which sulphosalts are the principal metallic minerals (Type I), and those in which sulphides predominate (Type II).

Type I is exemplified by ores from the shear-zones on the Rycon property and those in the large shear-zones on the Giant property contiguous to No. 2 shaft. Other ores which fall in this group, are those from minor shears on the Con property and from those shears on the Negus property which represent extensions of the Rycon shears. All samples, studied by the writer, from the Akaitcho property belong to Type II, however it has been learned from Mr. Boyle and the geologists of that property, that a more representative suite would show Type I affiliations.

Ores from Con C4 Shear, the Campbell Shear on the Negus property and the Cameron Shear on the Giant property, are of Type II. Ores from the Lynx and Captain properties also appear to belong to this group. However, the specimens obtained from these properties were collected at a relatively early stage in their development and may not be truly representative.

From the samples studied, ores of Type I are found principally in a gangue of quartz, which may, according to Boyle, be of at least three distinct ages. Stringers and segregations of carbonates occur in the quartz. The predominant metallic minerals are the soft, grey, sulphosalts, although sulphides (particularly pyrite, arsenopyrite and sphalertie) are present in appreciable amounts. Microscopically visible gold is more common than in ores of Type II and the particles in which it occurs are usually of larger dimensions.

The gangue for ores of Type II consists not only of quartz and carbonates but also sericitic schist. The principal metallic minerals are pyrite and arsenopyrite, with sphalerite and chalcopyrite in lesser amounts. sulphosalts are present, but neither in the quantity nor variety encountered in Type I. Gold, where present, is in fine disseminations.

Only three specimens from the Ptarmigan property were studied, an insufficient number to permit classification. No sulphosalts were observed in these samples, nor have they been seen in the field. The sulphides are of the same variety and relative abundance as those in other ores in the area, and their interrelationships appear to be the same. Gold occurs in one sample in several minute blebs, not in contact with the accompanying minerals.

MINERALOGY—PARTICULAR ASPECTS

In the succeeding sections, a number of theories are formulated concerning the relations of the metallic minerals to each other, and their paragenesis and mode of formation. These theories are postulated on the basis of the evidence available to date and hence represent only present probabilities. The author feels that hypotheses of this nature, which are within the realm of speculation, are justified even if they serve solely as a stimulus to further investigation.

The ores from the Yellowknife Bay area are very complex. Therefore. their paragenesis and mode of formation are probably also quite complex. To arrive at a positive conclusion as to the manner of their formation, study should be made of more samples having a wider distribution than those available to the writer. Until such a study is possible, the following observations and hypotheses may serve as a guide to an understanding of the mineralogy of this economically important area.

During the investigation, 23 ore minerals were identified which were introduced either prior to or during the period in which most of the gold was deposited. Besides these, there are five more metallic minerals which were probably formed at a much later time, and are presumably of supergene origin. Their occurrence is of little import in a consideration of the formation of the ores.

In his work on the mineralogy of the area, Ridland (1941) stated " . . . practically every polished section examined added another mineral to the list of species already recorded. In other words, if the number of sections studied had been doubled, the list of minerals would probably be increased substantially." The author does not agree with this. The great majority of minerals identified in the present study, were noted at a relatively early date, and further work served principally to confirm their presence and associations, but added relatively few new members to the existing array. More intensive investigations would doubtless result in a few additions but these would probably fit into the general pattern already established.

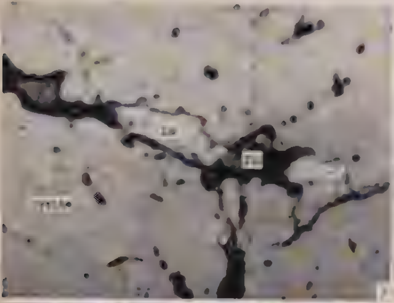
The present suite of ore minerals consists of a number of native elements, sulphides, sulphantimonites and antimonides, in which the metallic elements are Au, Fe, Cu, Zn, and Pb, with Ag and Sn present also in minor amounts. Presumably, any new addition would be composed of elements contained within the group: Au, Ag, Fe, Cu, Zn, Pb, Sn, Sb, As and S.

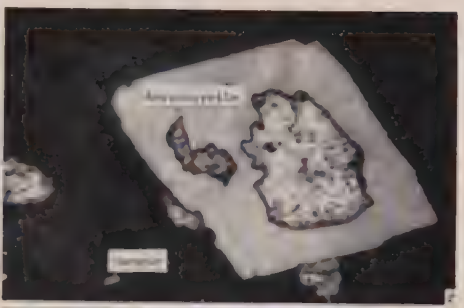
ORE MINERALS—DESCRIPTIONS AND RELATIONS

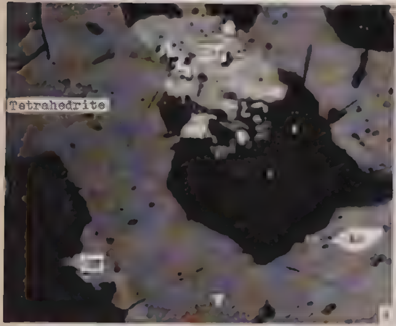
Pyrite, Arsenopyrite and Gudmundite

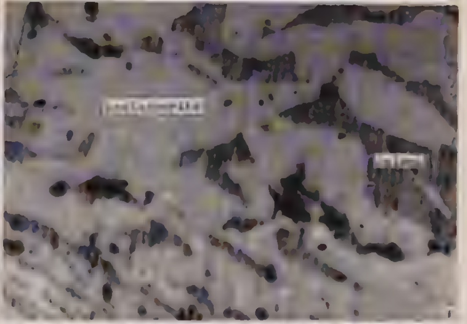
Pyrite is ubiquitous throughout the samples and is the most abundant metallic mineral. It occurs not only in the vein material, but also, in considerable amounts, in the adjoining wall rocks. Much pyrite in the ore zone is found in remnants of wall rock included in the quartz and carbonate vein material. Most of the pyrite is quite coarse-grained and exhibits development of crystal forms which, in many cases, have been modified either by fracturing and granulation, or else by partial replacement by gangue or later metallic minerals. A colloform and vuggy form occurs in specimens collected in proximity to late post-ore faults. This latter type is extensively replaced by or altered to marcasite, presumably through the action of late solutions circulating along the faults.

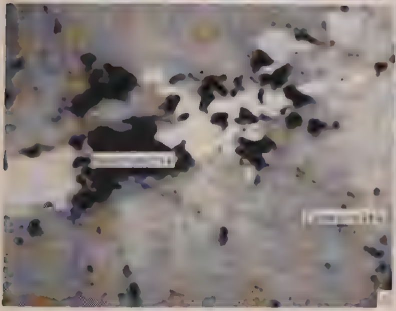
In all specimens where pyrite was noted in contact with other metallic minerals, the pyrite appears to be the oldest ore mineral present, with the exception of arsenopyrite. Remnants of pyrite are common within such minerals, or these minerals fill fractures within the pyrite (Fig. 1) or partially replace it. In some places, the age relations between pyrite and other metallic minerals are not apparent, but (again excepting arsenopyrite) in no case does the pyrite appear to be younger.











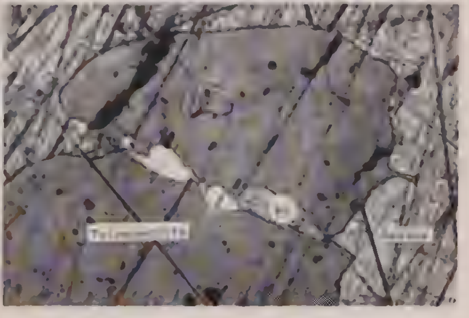


FIG. 1. Gold (Au) associated with jamesonite (Jm), veining pyrite, Rycon, vein EF, ×270.

FIG. 2. Gold replacing a crystal of arsenopyrite, Giant, first level, ×146.

FIG. 3. Tetrahedrite apparently invading chalcopyrite (Cpy) and gangue. The chalcopyrite probably was originally present as veins in the gangue and is evidently replaced to a greater extent than the gangue. Gold (Au) appears to be intimately associated with the tetrahedrite, Negus, vein 6, ×93.

FIG. 4. Galena, stained with $FeCl_3$, in boulangerite, Giant, 408 stope, ×134.

FIG. 5. Jamesonite, stained with KOH, veined by bournonite, Giant, 205 stope, ×122.

FIG. 6. Blebs of gold (Au) in a stringer of galena, stained with $FeCl_3$, which transects tetrahedite, Negus, 1399 stope, ×202.

Arsenopyrite, like pyrite, is a persistent mineral thoughout, but is quantitatively less important than the pyrite. Its two most common modes of occurrence are as well-formed diamond-shaped or rectangular grains, and as fine-grained granular masses.

In all observed instances, arsenopyrite appears to be older than all associated metallic minerals. It commonly forms euhedral inclusions within the younger minerals and in some cases such minerals are observed partially replacing grains of arsenopyrite (Fig. 2).

Gudmundite was identified in one sample only. It occurs as a fine-grained granular mass which may have been formed by the action of late antimony-rich solutions on a granulated mass of arsenopyrite. The occurrence of such masses of arsenopyrite within the same sample supports this idea.

Sphalerite, Chalcopyrite, Pyrrhotite and Stannite

Sphalerite, chalcopyrite, pyrrhotite and stannite appear to be closely associated. Sphalerite is the most prominant of these four minerals, but is commonly accompanied by one or more of the other three. Conversely, nearly all occurrences of chalcopyrite, pyrrhotite and stannite are accompanied by abundant sphalerite.

Much of the sphalerite observed has a broken appearance, and, when polished, plucks readily to give a rough, uneven surface. Sphalerite appears to be older, in time of formation if not in time of introduction of its constituents, than all other metallic minerals excepting pyrite and arsenopyrite. Chalcopyrite and pyrrhotite, which were probably formed from the same solutions as the sphalerite, appear to be slightly younger than sphalerite in time of formation. In most cases, the later metallic minerals occur as rims about associated sphalerite, but in some cases they are observed veining it or containing inclusions of it.

Most of the sphalerite is probably of the iron-rich variety marmatite. In hand specimens, it possesses a dark brown to black colour, indicative of an appreciable iron content. Much of the pyrrhotite observed in the samples occurs as fine disseminated blebs throughout the sphalerite, possibly formed by exsolution from an iron-rich sphalerite after its crystallization.

Chalcopyrite, in most instances closely associated with sphalerite, has two principal modes of occurrence—either in discrete bodies (Fig. 3), or in round or elongate blebs within sphalerite, commonly aligned along its cleavages. This latter occurrence is suggestive of an origin either by exsolution from sphalerite, or by preferential replacement of sphalerite along cleavage planes. Both mechanisms may have been operative; the disseminated blebs are more likely to have been formed by exsolution, whereas the aligned and elongated blebs and veinlets are more probably the product of replacement. Where larger bodies of chalcopyrite are observed in contact with sphalerite, the mutual relations either indicate contemporaneity, or else suggest that the chalcopyrite is the younger in time of solidification.

Zincian stannite[1] was found in only one specimen and in but minor amounts. Its association with other minerals was indeterminable, but its chemical composition and structure link it with sphalerite and chalcopyrite. This mineral probably accounts for much of the tin reported in assays of Yellowknife ores.

Galena

Galena appears to be closely associated with sulphosalts, and younger in age than all other sulphides except stibnite. It occurs alone or intimately associated with sulphosalts (Figs. 4, 6). In the latter association, galena appears to be either closely contemporaneous (Fig. 4) or slightly older. In a few instances, it appears to have formed at a slightly later date (Fig. 6), and embays or veins sulphosalts.

Stibnite

Stibnite was found in a few sections. It most commonly occurs as massive segregations in which are disseminated minor sulphosalts. In such samples, other sulphides occur only in minor amounts. The sulphosalts associated with such stibnite appear to have been formed contemporaneously or slightly later, possibly by reaction of stibnite with included sulphides. Native antimony is occasionally associated with massive stibnite and sulphosalts, and exhibits no definite age difference.

Some stibnite occurs in minor amounts in samples in which the relative abundance of sulphosalts to sulphides is high. In one sample, stibnite was noted in an intimate intergrowth with gold (Fig. 12). This occurrence will be dealt with in a later section.

In both modes of occurrence, stibnite appears younger than all associated sulphides since either it veins them or else they occur as remnants within it. Its age relations to the sulphosalts are indefinite, and it is probably either contemporaneous with them or slightly older. In no instance was it found in the vicinity of galena. Its presence is interpreted as indicating a localized high antimony-lead ratio in the mineralizing solutions, whereas the presence of galena suggests the opposite.

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[1] Determined by its powder diffraction pattern, which is similar to that of stannite but exhibits the slight expansion of the zincian variety.

The Sulphosalts

Sulphosalt associations, both among themselves and with the sulphides, exhibit certain uniformities in the Yellowknife ores.

All sulphosalts observed in these ores are sulphantimonides. No true sulpharsenides have been identified by *x*-ray powder diffraction methods. Some of the tetrahedrite appears to be arsenical and grading into tennantite;[1] this is possibly the result of absorption of arsenic from arsenopyrite.

Where more than one sulphosalt appears in one specimen, the varieties present usually have some chemical similarity. Meneghinite was noted only in samples containing considerable galena, boulangerite or both. This suggests that meneghinite is able to form only in an environment in which lead is abundant, and in which the ratio of antimony to other metallic ions is low (Table 1). Zinkenite was found in specimens in which neither galena nor boulangerite occur, and in which stibnite is commonly found. This suggests that a favorable environment for zinkenite is one in which the ratio of antimony to other metallic ions is high.

The sulphosalts appear to have a chemical similarity to the associated pre-existing metallic minerals. Tetrahedrite is commonly associated with chalcopyrite (Fig. 3) and appears to replace it. Chalcostibite was found only where there were older copper minerals, as was commonly bournonite. Berthierite occurs principally with abundant pyrite or arsenopyrite. These associations suggest that some of the constituent metallic elements of the suphosalts, were present before the introduction of the solutions from which these minerals formed. Much of the sulphosalts may have been formed by reaction of pre-existing sulphides with an antimony-rich fluid.

All the sulphosalts seem close in age of formation, although minor apparent age differences are noted (Figs. 5, 7, 8). Jamesonite, which is most abundant, commonly appears to have been deposited at an earlier time than the others (Figs. 5, 8). This suggests that jamesonite may form more readily than the other sulphosalts, and hence would tend to form first from the antimony-rich solutions, with the varieties of subsequent sulphosalts formed, dependent on the residual constituents available.

Unlike the sulphides, the sulphosalts exhibit little evidence of having been subjected to differential stresses. Whereas the sulphides are commonly fractured and granulated, the sulphosalts exhibit only minor

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[1] From the Captain property in the North part of the area, which may have a different mineralogy than the properties to the South. Also, some tetrahedrites from wall rocks of the Giant and Negas properties, appear to be arsenical on the basis of dimensions of their unit cell.

TABLE 1. CHEMICAL ASPECT OF YELLOWKNIFE ORE MINERALS

Mineral	Formula	Other Metal Atoms	Mol % S	Metal Ions
		Sb		
Gold	Au		0.0	Au
Aurostibite	$AuSb_2$	1:2=0.5	0.0	Au
Antimony	Sb	0:1=0.0	0.0	Sb
Stibnite	Sb_2S_3	0:1=0.0	60.0	Sb
Pyrrhotite	$Fe_{1-x}S$		50.0−	Fe
Pyrite	FeS_2		66.7	Fe
Marcasite	FeS_2		66.7	Fe
Arsenopyrite	FeAsS	1:1[1]=1.0	33.3	Fe
Gudmundite	FeSbS	1:1=1.0	33.3	Fe
Berthierite	$FeSb_2S_4$	1:2=0.5	57.2	Fe
Chalcocite	Cu_2S		33.3	Cu
Covellite	CuS		50.0	Cu
Chalcostibite	$CuSbS_2$	1:1=1.0	50.0	Cu
Sphalerite	ZnS		50.0	Zn
Lead	Pb		0.0	Pb
Galena	PbS		50.0	Pb
Zinkenite	$Pb_6Sb_{14}S_{27}$	3:7=0.43	57.4	Pb
Semseyite	$Pb_9Sb_8S_{21}$	9:8=1.12	55.3	Pb
Boulangerite	$Pb_5Sb_4S_{11}$	5:4=1.25	55.0	Pb
Meneghinite	$Pb_{13}Sb_7S_{28}$	13:7=1.86	58.4	Pb
Chalcopyrite	$CuFeS_2$		50.0	Cu:Fe=1:1
Tetrahedirte	$(Cu, Fe)_{12}(Sb, As)_4S_{13}$	3:1[1]=3.0	44.6	Cu:Fe=1:1[2]
Stannite	$Cu_2(Zn, Fe)SnS_4$		50.0	Cu:(Fe,Zn):Sn=2:1:1
Jamesonite	$Pb_4FeSb_6S_{14}$	5:6=0.83	56.0	Pb:Fe=4:1
Bournonite	$PbCuSbS_3$	2:1=2.0	50.0	Pb:Cu=1:1

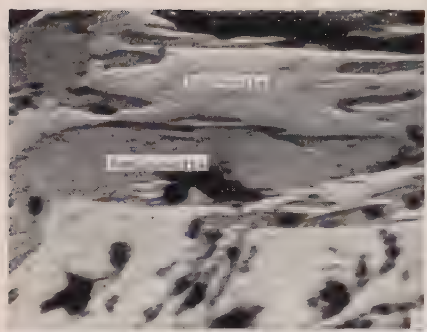
[1] One atom of As is considered the equivalent of one atom of Sb.

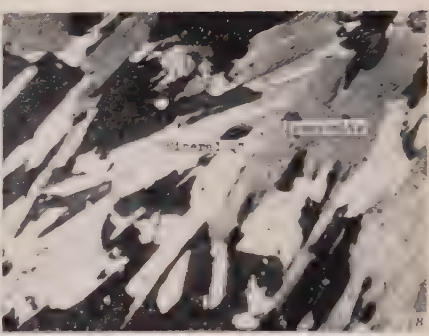
[2] An approximation.

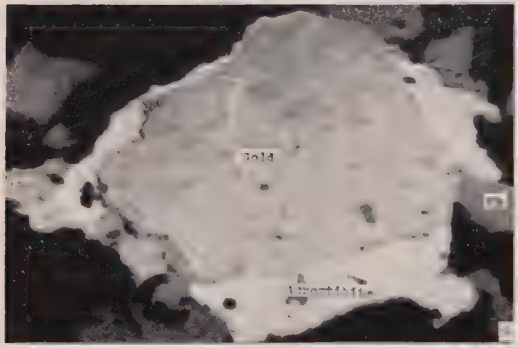
evidences of strain. Under polarized light, some grains of anisotropic varieties have a wavy extinction similar to that exhibited by strained quartz. This, plus the occurrence of considerable polysynthetic twinning, suggests that the sulphosalts were subjected only to minor stresses.

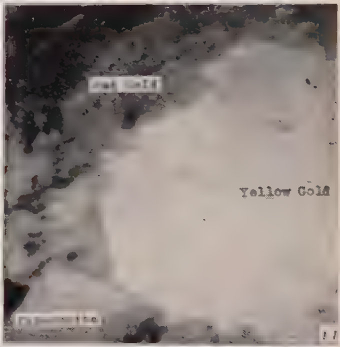
Gold

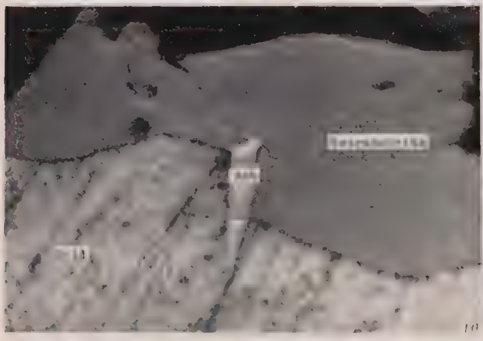
Native gold occurs throughout the area. It appears to be closely associated with the sulphosalts although, in many cases, it embays them and is hence probably slightly younger. The quantity of visible gold is greatest in those specimens in which sulphosalts are most abundant, and in which they have the lowest ratio of other metallic ions to antimony (Table 1). Other minerals commonly associated with gold are aurostibite, arseno-











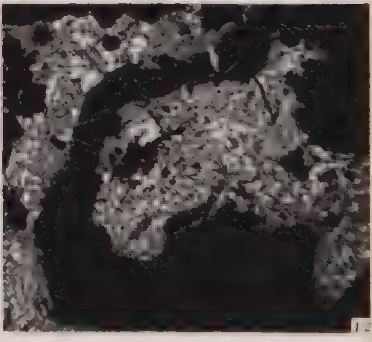


FIG. 7. Intergrowth of bournonite and boulangerite, stained with HCl fumes, Giant first level, ×81.

FIG. 8. Intergrowth of jamesonite, stained with KOH, and "Mineral Q," Giant, Brock Zone, ×81.

FIG. 9. Gold rimmed by aurostibite, in a vein of tetrahedrite (Th), Rycon, shear 57, ×202.

FIG. 10. Aurostibite (Asb) transecting a contact between gold and tetrahedrite, Rycon, shear 57, ×263.

FIG. 11. Yellow gold, rimmed by red gold, in jamesonite, Rycon, shear 51, ×182.

FIG. 12. "Purple Gold"—a fine intergrowth of stibnite (grey) and gold (white), Rycon, shear 54, ×284.

pyrite and sphalerite. The gold appears to be of more than one variety, and of possibly more than one depositional age. One variety (Type 1), which possesses a light yellow colour and hence is probably richer in silver, seems to be older than the others.

The most abundant type of gold (Type 2) has a rich yellow colour. It occurs deposited on crystal faces of arsenopyrite (Fig. 2), as blebs in sulphosalts (Fig. 6), as fairly coarse grains within the sulphosalts (Figs. 9, 10, 11) or within sulphides (Fig. 1), and as discrete particles in the gangue. Much Type 2 gold has aurostibite intimately associated with it (Figs. 9, 10).

The third variety (Type 3) has a reddish hue. This may be due to some dissolved copper, as suggested by Ferguson (1950), and this type is found only in the neighbourhood of copper minerals. "Type 3" was found only in samples containing "Type 2," and in most cases is closely associated with this variety. Contacts between these two varieties (Fig. 11), although indistinct, suggest that "Type 2" is the younger.

Spectrographic analyses were made of the different gold types but the results were inconclusive. A pure sample could not be obtained due to the close associations of "Type 2" and "Type 3" and the proximity of most of the gold particles to sulphosalts. The spectrographic analyses do, however, suggest that "Type 1" is considerably richer in silver than the other two varieties.

In several samples a purple mineral occurs, which was identified by *x*-ray powder methods as gold, suggesting still another variety of this mineral. However, on closer examination at high-power magnifications, this material proved to be an intimate, blotchy, intergrowth of gold and a grey anisotropic mineral identified by *x*-ray examination of the mixture as stibnite (Fig. 12). In the same samples aurostibite occurs associated with gold. Possibly, "purple gold" was formed by the reaction of some later sulphur-rich solution with aurostibite. It is postulated that antimony possesses a greater affinitity for sulphur than for gold. This would result in the formation of stibnite accompanied by the precipitation of gold, when aurostibite comes in contact with excess sulphur.

Aurostibite

Aurostibite was observed only in the presence of "Type 2" gold. It occurs principally as rims on gold particles (Fig. 9), as extensions of gold grains, or along contacts between gold and other minerals. In a few cases, it veins other minerals in the neighbourhood of gold particles or even veins gold itself (Fig. 10).

The age relations between gold and aurostibite are commonly not clear-cut except where aurostibite veins gold. The formation of aurostibite[1] probably begins while gold is still being deposited, and continues for a short while after all the gold has formed.

Lead and Antimony

Native lead and antimony were found in minor quantities in specimens from a number of localities. Lead occurs in samples in which minerals containing a relatively low percentage of sulphur are abundant. It exhibits no significant relations with other minerals and is usually in discrete particles in the gangue. Native antimony was observed only as small grains in massive stibnite.

These two native elements are believed to indicate solutions somewhat deficient in sulphur. Most reported occurrences of native lead are regarded as supergene. Its presence in Yellowknife ores at a depth of 500 feet suggests that such a theory is not tenable in this case. Antimony also appears to be a product of hypogene mineralization, since it occurs at depths up to 750 feet. The specimens in which both these minerals occur are quite fresh in appearance, and exhibit no evidence of supergene mineralization. Shannon (1927) reports an instance where native lead is the principal ore mineral of a lead deposit, which is almost certainly of hypogene origin.

Secondary mineralization

Secondary minerals observed in the area include marcasite, chalcocite, cassiterite, limonite, malachite and azurite.

Marcasite occurs in appreciable amounts in the neighbourhood of late post-ore faults, and also in surface and near-surface specimens. In each case, it appears to be the youngest metallic mineral present, and is probably either a product of late solutions circulating along post-ore faults, or else of secondary sulphide deposition near surface.

Chalcocite was noted in a number of surface and near-surface samples. It occurs in fine stringers which transect copper-bearing minerals. Such chalcocite is more extensive in sulphosalts than in chalcopyrite. It is believed that all the chalcocite was produced by solutions, probably supergene in origin, which circulated through the ores at some time subsequent to the last period at which they were formed.

Sphalerite, possibly of secondary origin, is found in a number of localities in this area. This sphalerite forms small stringers which transect the other metallic minerals. It seems probable that both chalcocite and this sphalerite were formed during a period of secondary sulphide mineralization.

Cassiterite occurs in one weathered specimen, obtained from a surface trench, associated with sphalerite and intermixed with marcasite. Its occurrence in a weathered sample of ore suggests that it was formed as a product of secondary alteration of some pre-existing stannite. Its occurrence in the neighbourhood of sphalerite supports this idea.

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[1] This mineral is treated at greater length in a succeeding section.

Limonite, malachite and azurite were all noted in hand specimens from surface outcroppings of the veins. They appear to have been formed as a product of recent weathering.

METALLIC MINERALIZATION IN THE WALL ROCKS

Samples of wall rocks collected in the vicinity of the orebodies contain some of the metallic minerals which occur in the ores. Pyrite and arsenopyrite are usually present, accompanied, in places, by minor amounts of sphalerite and chalcopyrite. Galena and sulphosalts occur in minute disseminated particles in a few samples.

From evidence of movement noted in the field, and from microscopic textures of the metallic minerals, it seems reasonable to consider dilation of the rocks the principal factor causing the introduction of the mineralizing solutions. During each period of deformation or movement, the same stresses would act on all rock types. The various members would, however, possess different physical properties and hence their response to deformation would be varied. Differences of response to the same stress could produce marked differences in dilation of the various members, and thus act as an important factor in localizing the introduction of mineralizing fluids.

Quartz-carbonate veins would, expectably, become more dilatant than a schistose shear zone, when both are subjected to the same deformation. Evidence of more than one introduction of gangue, as reported by Boyle (1952), suggests that the size of the veins with respect to the enclosing shear zones, was increasing with each successive period of mineralization. If this was the case, the ratio of dilatability within the veins to that within the surrounding schists, would increase with each successive mineralization period, and hence later minerals would be confined more and more to these veins.

PARAGENESIS

In the paragenesis of the Yellowknife ores, the following periods of mineralization are postulated, with the oldest first:

1. A solution rich in sulphur, iron and arsenic, was introduced from which arsenopyrite and pyrite formed. Much of the arsenopyrite was formed before deposition of pyrite commenced.

2. A solution rich in sulphur, zinc, iron and copper, and containing minor tin was then introduced. It may have been relatively free of iron,

with the iron contained in minerals formed at this time, being derived from pre-existing pyrite and arsenopyrite.

Sphalerite was the first mineral to be formed from this solution, followed by chalcopyrite, pyrrhotite and stannite. Some of the chalcopyrite and pyrrhotite associated with the sphalerite, may represent exsolved material, but some may have resulted from the reaction of residual solutions with sphalerite.

3. There was, possibly, an early introduction of gold. If such a period did occur, the gold formed was a light coloured variety (Type-1), rich in silver.

4. An antimony-rich solution was then introduced, which contained sulphur, gold, silver and lead, and possibly some copper and iron. Much of the iron, copper and arsenic contained in minerals formed at this time may have been derived from pre-existing metallic minerals during the processes of replacement.

Evidence from polished sections indicates that there may have been more than one deposition of gold during this period. If this is so, gold of Type 3 was probably formed early in the period. Its formation may have been caused by the reaction of the solutions with pre-existing metallic minerals on first reaching the site of ore-formation, with incorporation of copper producing the red colour of this gold.

Galena and stibnite were probably formed during this period wherever the available supply of antimony or of lead, was insufficient for the formation of sulphosalts.

No uniform paragenesis was found for the galena, stibnite and sulphosalts within this major period. The varieties of minerals formed in any one place, and their order of formation, was probably a function of the concentrations of the constituents available for mineral formation. Differences in available proportions of those constituents which could not have been derived from pre-existing minerals, may have been caused by a filtering effect imposed on the solutions by impounding structures. Differing degrees of dilation throughout the host quartz-carbonate veins, accompanied by varying degrees of mobility of the solution constituents, is a possible alternative.

Aurostibite and gold of Type 2 probably formed late in this period, with aurostibite forming shortly after the gold by reaction with excess antimony. Native lead and antimony were probably among the last minerals to form, and indicate an appreciable deficiency of sulphur during the later stages of mineralization.

5. Late faulting accompanied or succeeded by circulation of supergene or hypogene solutions, caused the formation of a second age of sulphides.

THE ORE-FORMING FLUIDS—THEIR CHARACTER AND EMPLACEMENT

The mineralizing fluids seem to have been of a hydrothermal type similar to those postulated by Graton (1940) and Neumann (1948). That the mineralization appears to have taken place by the introduction of several successive solutions of differing compositions, agrees with Neumann's idea of "endomagmatic hydrothermal differentiation." The wall rocks adjoining the ore deposit show no definite evidence of either acidic or alkalic alteration associated with the emplacement of the metallic minerals. The presence of large quantities of carbonates in the ores does suggest that the solutions may have been alkaline.

The manner in which the gold was transported, is uncertain. It may have been transported in the form of a sol, or in true solution, either as gold or as a salt. The affinity of gold for antimony, as evidenced by its ability to combine with antimony, suggests that the gold might be transported as a soluble antimonide complex. Since aurostibite reacts readily with both nitric and hydrochloric acids, and with potassium hydroxide, it would probably be equally soluble in both acidic and alkalic solutions.

The manner of emplacement of the ore-forming fluids seems quite clear. In each instance of introduction of a solution, there is evidence that deformation or movement took place previously, and subsequent to the formation of the pre-existing minerals. Any movement or deformation of the brittle veins in which these ores occur, would undoubtedly be accompanied by dilation, which would serve as an adequate mechanism to initiate the introduction of the ore-forming fluids.

This type of deposit appears to be a combination of filling of zones of dilation and of replacement. Ore minerals fill fractures in gangue as well as in earlier metallic minerals, and, in addition, show many manifestations of replacement processes.

AUROSTIBITE—ITS OCCURRENCE AND IMPLICATIONS

Aurostibite is of particular interest mineralogically, not only for its novelty as a mineral species, but also because of the economic and mineralogical implications of its occurrence.

This mineral was first described by Graham & Kaiman[1] (1952). Crystallographically, it is a member of the pyrite group, and the unit cell contains Au_4Sb_8, with $a = 6.659 \pm 0.003$A. In polished section it has a hardness of C−, is isotropic and has an extreme white colour which gives it a slightly pinkish appearance in contrast with galena. The standard etch reactions in the order of reactivity are: HNO_3, $FeCl_3$, HCl, KOH positive; $HgCl_2$ and KCN negative. It occurs, intimately associated with gold, late in the paragenetic sequence, and, in many instances, appears slightly younger than the gold.

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[1] Geological Society of America, Annual Meeting, November 1951.

This mineral has considerable economic significance. Not only does it represent a new naturally occurring gold compound, but its relative insolubility in a cyanide solution poses important recovery problems. The fact that it armours gold is many occurrences, would, as Graham & Kaiman (1952) have mentioned, cause losses in ordinary cyanide mill-circuits, out of all proportion to the amount of gold actually present in the mineral itself. Furthermore, the possibility that this cyanide-resistant mineral may actually be synthesized in roasting ores of the Yellowknife type has to be considered.

Mines in the Yellowknife Bay area, in the past, have reported relatively high losses in their gold recoveries. At least some of such losses may be due either to the presence of aurostibite, or to its formation during roasting.

Summary and Conclusions

The gold deposits of the Yellowknife Bay area represent a type different from those found elsewhere in the Precambrian Shield of Canada. The intimate occurrence of gold with sulphosalts rich in antimony, has not been reported in this country, and is quite different from its more common association with tellurides. In Yellowknife ores, tellurium appears to be virtually absent.

Because of their novelty , the depths to which these deposits should extend are not known. High formational temperatures seem improbable, although a depositional environment having temperatures in the order of several hundred Centigrade degrees is quite plausible. The mines in this area have, in several instances, reached mining depths exceeding one thousand feet and, so far as is known, the gold values show no significant change.

Further study of the chemical and mineralogical relationships between gold and antimony should prove of great interest and economic significance. If ores of this type are to be treated efficiently, such research is of great importance.

A number of conclusions may be drawn from the present investigations which, although hypothetical due to the scope of the study, appear reasonable:

1. Gold exhibits a close affinity with relatively low temperature minerals rich in antimony. The quantity of microscopically visible gold present in any one locality, appears to be greatest where such minerals are abundant.

2. Although the mineralogy is quite complex, its chemical constituents

fit into a relatively simple pattern. Any additions to this array should be composed of these elements.

3. The formation of the Yellowknife ores took place in a number of successive stages, with minerals formed during each period incorporating elements from earlier formed minerals.

The postulation of replacement as the mode of origin of an ore deposit has, in many instances, produced the criticism that this would require not only the introduction, but also the removal of material. The idea that much of the material which was apparently replaced, was in reality incorporated into later minerals, helps satisfy any such objection.

4. The paragenetic sequence of the period in which gold and sulphosalts were formed, is not definite. The minerals formed at this time exhibit numerous reversals in age relations. The order in which they were deposited in any one locality was probably a function of the concentrations of minerals constituents that were present at that place.

5. The ores have been formed by filling of zones of dilation accompanied by some metasomatic replacement.

6. Mineralogical investigation indicates that dilation accompanying deformation was an important factor in controlling the emplacement of these ores.

7. Investigations of complex ores, particularly those containing sulphosalts, are greatly facilitated by *x*-ray powder studies. Identification by etch reactions and microchemical tests is unreliable with ores of this character.

APPENDIX—"MINERAL Q"

In one specimen, a grey acicular metallic mineral was noted, whose *x*-ray powder spectrum did not correspond to that of any reported mineral. This mineral is tentatively referred to as "Mineral Q."

The type locality for this mineral is a surface trench on the Brock Zone of the Giant property. It occurs as discrete needles in gangue and intimately associated with jamesonite (Fig. 8), in specimens of ore in which pyrite and arsenopyrite are also present. It seems to be slightly later in time of formation than the jamesonite since blades of it transect intergrain boundaries of jamesonite.

Due to its intimate association with jamesonite, no chemical analysis of this mineral was possible. A very small amount was obtained for a spectrographic analysis, which indicated the presence of the following elements in probable order of decreasing importance: Fe, Cu, Sb, Pb, Ag.

A single crystal fragment of this mineral was obtained from the polished section for *x*-ray measurements. Owing to its acicular habit, only one axis of adjustment was available. This direction of elongation proved to be the crystallographic *b*-axis of a monoclinic lattice.

Rotation and Weissenberg films about the axis of elongation yielded the lattice dimensions:

$$a = 19.06 \text{ A}, \quad b = 4.11 \text{ A}, \quad c = 17.26 \text{ A}, \quad \beta = 95°50'$$

No systematic omissions of diffractions were observed, therefore the space group is *P*2/*m*, if the class is holohedral.

The *x*-ray powder spectrum for "Mineral Q" is:

I	θ(Cu)	*d*(meas)	*I*	θ(Cu)	*d*(meas)	*I*	θ(Cu)	*d*(meas)
s	12.2°	3.65 A	w	15.45°	2.89 A	m	22.1°	2.05 A
vs	13.3	3.35	s	16.05	2.79	m	24.2	1.881
m	14.3	3.12	vw	17.1	2.62	w	25.4	1.797
vw	14.9	3.00	w	20.25	2.23	w	26.65	1.719

The appearance, associations and lattice dimensions of "Mineral Q" suggests that it is undoubtedly a sulphosalt. The existence of a new monoclinic sulphosalt in which the *b*-axis is the axis of elongation, is of some interest. None of the well-established monoclinic sulphosalts have their direction of elongation parallel to the *b*-axis. There are, however, two cases in which such minerals have been reported and it is of further interest that, in both cases, the cell elements of these minerals were very close to those of "Mineral Q."

Berry (Peacock & Berry, 1940), reports the presence of one such mineral in an intimate intergrowth with another mineral having a platy development. This intergrowth had originally been named "seleniferous galenobismutite." The other of these minerals is an artificial sulphantimonite (Phase II with Pb:Sb=3.4:5.4) which was synthesized by Robinson (1948). He believed that this synthetic material and the Pb, Bi, Se, S mineral reported by Berry, might be isostructural. It is possible that "Mineral Q" is also isostructural with these two minerals.

The rotation and Weissenberg *x*-ray films of Robinson's phase II and Mineral Q are essentially identical in position and intensity of diffractions, they differ markedly in the shape of the spots.

The cell dimensions for these three minerals are:

	Mineral Q	Robinson (1948)	Peacock & Berry (1940)
a	19.06 Å	19.20 Å	18.07 Å
b	4.11	4.13	4.05
c	17.26	17.43	17.57
β	95°50′	96°24′	94°29′
Space group	*P*2/*m*	*P*2/*m*	*P*2/*m*

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ON THE COLOUR OF BLACK AND GREY QUARTZ FROM YELLOWKNIFE, NORTHWEST TERRITORIES, CANADA[1]

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ABSTRACT

Heating tests, chemical tests, and *x*-ray analysis have shown that the colour of black and grey quartz, occurring in veins and lenses in the greenstones and sediments of the Yellowknife gold belt, is primarily due to disseminated carbon and graphite. Finely divided sulphides or other dark minerals may be responsible for a partial darkening of the quartz, but these impurities are secondary in effect to those of carbon or graphite.

INTRODUCTION

The colour of quartz has engaged the attention of many investigators, and satisfactory hypotheses have been given for the cause of the colouring in amethyst, rose, and smoky varieties. Some work has been done on the nature of the colouring medium of black and grey quartz, but in general the hypotheses advanced have received little rigorous investigation.

The research work outlined in this paper completes one portion of a general investigation of the colour of quartz from Yellowknife and other Canadian localities. The work described here was started in the Geochemical Laboratory at the University of Toronto under the supervision of Professor F. G. Smith, and completed in the laboratories of the Geological Survey of Canada.

GEOLOGICAL OCCURRENCE AND DESCRIPTION OF THE BLACK AND GREY QUARTZ

The gold quartz veins of the Yellowknife region occur in folded and faulted greenstones and sediments of Archaean age. Two periods of faulting are clearly represented in the greenstones of the region. The first period produced an extensive series of shear zones which contain the economic gold quartz veins and lenses; the second is represented by narrow breccia faults containing a few quartz lenses which have no economic interest. In the highly folded sediments quartz veins and lenses occur in small faults, along broken axial planes of isoclinal folds, in drag folds, and along bedding planes. Narrow breccia faults belonging to the same age and structural pattern as those noted above in the greenstones are widespread. For a more detailed account of the geology of the area the

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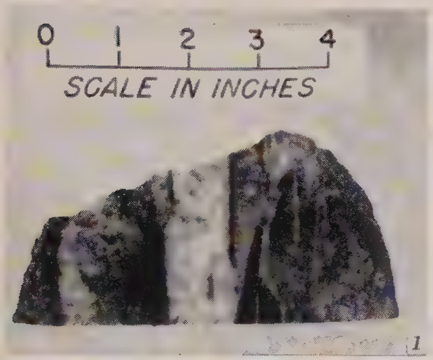

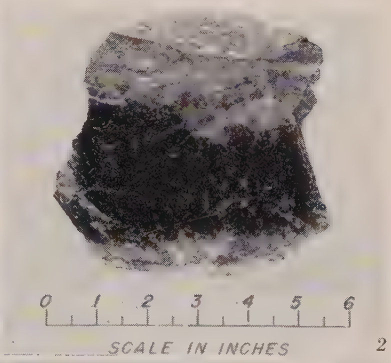

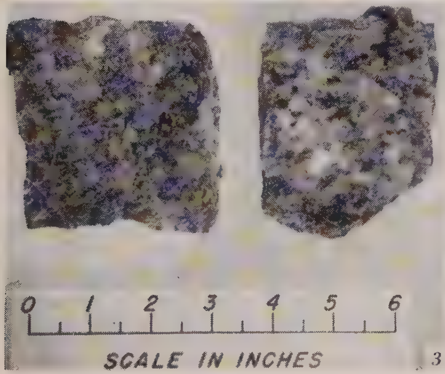

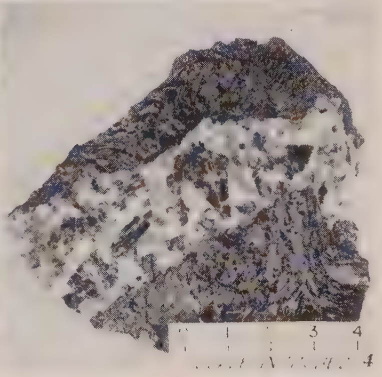

Fig. 1. Black quartz cut by veinlets of white quartz. Rycon mine Yellowknife, N.W.T.

Fig. 2. Black quartz occuping the central portion of a quartz vein. Specimen shown was taken across width of quartz vein. Negus mine, Yellowknife, N.W.T.

Fig. 3. Mottled quartz. Rycon Mine, Yellowknife, N.W.T.

Fig. 4. Black calcite enclosed in white quartz with adjacent walls of chlorite-sericite schist. Giant mine, Yellowknife, N.W.T.

reader is referred to the published accounts of Henderson and Brown (1950), and Jolliffe (1938).

In the greenstones the early shear zones contain two main types of quartz, an early, grey to black variety and a later, white to light flesh-coloured variety. Locally, the two types contain pyrite, arsenopyrite, stibnite, boulangerite, jamesonite, several other sulphosalts, and gold.

Black quartz is characteristic of a set of parallel shear zones on the properties of the Negus and Rycon gold mines, but has been noted in many other localities, especially in some of the underground workings of the Giant mine. It occurs in narrow lenses and veins within the shear zones and appears to have formed both by open space filling and replacement.

In the veins and lenses the black quartz is distinctly early and is cut by the later generation of white quartz (Fig. 1). In some lenses black quartz or grey quartz is adjacent to the vein walls with the white variety occupying a medial position; in other veins the reverse may be true (Fig. 2). Many veins and lenses contain a mottled variety which consists of small nuclei of black quartz in a matrix of white quartz (Fig. 3). Mottled varieties grade by degrees into dark grey to light grey varieties. In general, a wall rock alteration accompanies the black, grey, and mottled varieties of quartz. The minerals present in the altered zone are ankerite, chlorite, sericite, arsenopyrite, and pyrite. Locally, grey to black ankerite, calcite, and dolomite (Fig. 4) occur in association with the black and grey quartz. The age relationship of this carbonate is difficult to determine since many ages are usually present. In some cases the carbonate is early, and probably originated in part by a recrystallization of the carbonate formed in the wall-rock alteration zones; in other cases the black carbonate fills vugs containing euhedral quartz crystals.

In hand specimens the black quartz may grade to grey quartz in a single specimen. Other specimens are common in which the quartz is a dense coal black colour that, in appearance, resembles anthracite coal. In many veins and lenses the black and grey quartz has undergone severe crushing and brecciation and subsequent healing by white calcite.

Thin sections of the black quartz reveal a groundmass of medium-grained quartz intersected and surrounded by a ramifying system of veinlets and patches of fine-grained quartz. Inclusions and strain extinctions are notable in the medium-grained quartz, whereas, the fine-grained variety is usually clear and possesses sharp extinction. The black colouring material lies along an intersecting gridwork of pronounced inclusion planes that are restricted to the medium-grained quartz. These inclusion planes appear to be secondary features that may have formed after the consolidation of the quartz, but another origin is possible since these planes of colouring matter may be residuals after replacement of the black carbonate described below.

Thick sections studied under the binocular microscope give a better idea of the nature of the colouring material. In these sections the colouring material is seen to lie along a network of wavy planes that intersect the medium-grained quartz at many angles and are terminated against the clear veinlets and patches of fine-grained quartz. The density of the colour is dependent upon the quantity of these intersecting planes.

The black ankerite, calcite, and dolomite are found locally in many of the shear zones of the region. In some localities the carbonate exhibits good euhedral crystals which have a marked depositional banding due to the alternation of colourless or white bands with grey or black bands. The majority of the carbonate is, however, intersected by a mesh of

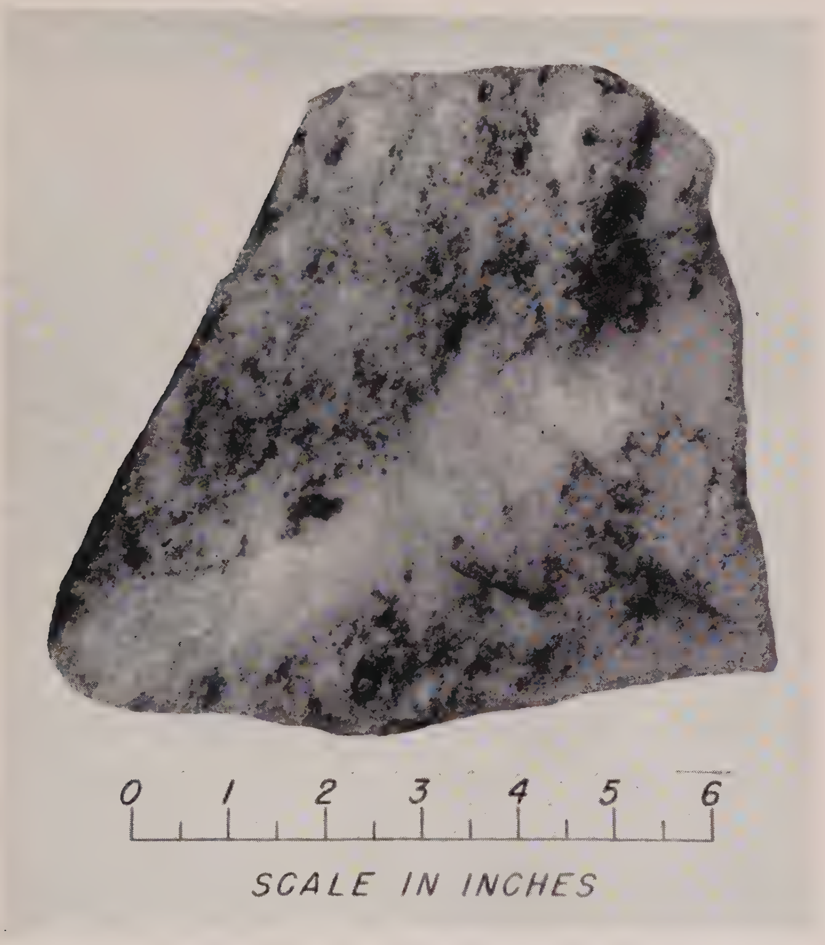

FIG. 5. Early grey quartz cut by later white quartz. Ptarmigan mine, Yellowknife, N.W.T.

dark grey or black seams and planes of colouring material. Again, the density of the black colouring is dependent on the quantity of the seams and planes. As noted above, this carbonate is apparently replaced by both grey and black quartz, but in some localities white quartz appears to replace the carbonate.

The veins and lenses in the sediments exhibit two distinct ages of quartz. The first age is a grey quartz, and the second cutting age is a white quartz (Fig. 5).

In hand specimens the quartz is relatively pure and contains only minor quantities of pyrite, sphalerite, and galena. In thin sections the grey quartz exhibits a ground mass of medium sized grains cut by ramifying areas of small quartz grains. The medium sized grains of the grey quartz contain innumerable microscopic black ovoid specks which show no preferred orientation or location.

Identification of the Colouring Matter

It was thought at first that the black and grey colour was due to electronic darkening produced by radioactivity similar to that suggested by Holden (1925) and others as the cause of the colour of smoky quartz. To test this hypothesis specimens of black and grey quartz were heated with a specimen of smoky quartz made available by Dr. F. G. Smith. The tests were conducted in a small electric furnace, and the temperatures were recorded by a thermocouple. The results of this experiment are given in Table 1.

Table 1. Heating Test on Black and Smoky Quartz

Temperature ° C.	Colour of Smoky Quartz	Colour of Black & Grey Quartz
100	Dark brown to smoky brown	Black, grey
200	No change	No change, grey
300	Slight bleaching	No change, grey
350	Almost completely bleached	No change, grey
400	Completely bleached, colourless, many factures	No change, many fractures
500	Completely bleached, colourless, many fractures	No change, many fractures
600	Completely bleached, colourless, many fractures	Slight bleaching on edges, many fractures
700	Completely bleached, colourless, many fractures	Slight bleaching on edges, many fractures
800	Completely bleached, colourless, many fractures	Slight bleaching on edges, many fractures
1,000	Completely bleached, colourless, many fractures	Slight bleaching on edges, many fractures

Heating rate—10° C. per minute.

Specimens were allowed to cool after attaining each temperature indicated in the table and comparisons of the two types were made.

After cooling the specimens from 1,000° C. to room temperature the smokly variety remained clear and colourless, but the black and grey varieties presented only a slightly bleached appearance on thin edges, and the interior remained relatively unaffected. Heating the black and grey quartz at 1,000° for four hours had little effect in removing the body colour.

Since these experiments failed to give a clue to the nature of the colouring medium, it was decided to dissolve specimens of the black and grey quartz in hydrofluoric acid and examine the residues. For these experiments 500 grams of black and grey quartz were prepared in chip form, dissolved, and the residues examined. They were seen to consist of fine grey sulphides, some pyrite, gold, a few unidentified, colourless euhedral crystals, and an abundant black substance in the case of the samples of black and grey quartz from the greenstone area, and of some pyrite and an abundant black substance in the case of the samples of grey quartz from the sedimentary area. These residues were then successively leached with hydrochloric acid, nitric acid, and aqua regia for one hour. The solutions after this treatment were visibly darkened by extremely fine black material. After settling, decantation, and thorough washing, the black material was caught on watch glasses, and x-ray photographs were taken.

In the majority of cases of the quartz from the greenstones the black material failed to give an x-ray powder pattern for graphite due probably to the finely divided state of the material. In two separations, however, x-ray patterns for graphite were obtained. Ignition tests carried out on platinum foil showed that the finely divided black material burned leaving no residue. Preliminary tests conducted on this material to determine the presence of hydrocarbons proved negative. It was concluded in view of this evidence that the colouring medium in most cases was finely divided carbon and in some cases graphite. Further work is proceeding on the material which failed to give the graphite pattern.

In all separations of the black material from the quartz of the sedimentary area, x-ray powder photographs gave consistent graphite patterns and further chemical tests were not necessary.

Similar experiments were carried out on the grey and black carbonate from the main occurrences at Yellowknife. In all cases the colouring matter was carbon and failed to give x-ray powder patterns of graphite.

To test the general validity of carbon and graphite being the colouring medium in black quartz, specimens from other regions of the Precambrian in the Northwest Territories, from the Red Lake region in Ontario, and from the O'Brien Mine in Quebec were tested with the same results as those obtained from the Yellowknife quartz. Further work is proposed on the quartz from other areas when samples become available.

Samples of white quartz, milky quartz, and light flesh-coloured quartz from the Yellowknife veins were treated in a similar manner to that of the black quartz, but carbon or graphite was not present in any of the samples.

DISCUSSION

Two general ideas have been prevalent in the minds of those who have examined the problem of the colouring of black and grey quartz. The colour has been attributed to: (I) Electronic darkening due to the action of radioactive emanations—the view advanced by Bruce (1934). (II) Impurities: these may be finely disseminated sulphides, tourmaline needles, various dark minerals, carbonaceous matter, graphite, etc.—in general, the colour is attributed to impurities, and usually some mineral is suggested, but few qualifications are made.

In the cases studied by the author the first postulate does not apply because it has been shown that a heating comparison of black and grey quartz and smoky quartz has proved conclusively that the phenomenon cannot be attributed to the action of radioactivity. There are several other arguments against the radioactivity postulate. At Yellowknife the veins and wall-rocks are very low in radioactivity, and hence, no actuating mechanism is present to produce radioactive darkening. Black coloration in carbonate is not produced by radioactive processes; the colour produced is generally some combination of red. Finally, where black, grey and white quartz occur in an intimate relationship there is no reason to suspect that one age of quartz would be affected by radioactivity and not the other.

The second cause, that attributed to impurities, probably is responsible for most of the black and grey quartz that is so common a feature of the gold-quartz veins of the Precambrian Shield. Disseminated sulphides may act as a colouring agent since in the experiments described in this paper finely divided sulphides were isolated from the residue after leaching with hydrofluoric acid. In several experiments, however, sulphides were not present yet the quartz presented a coal black colour. It is, therefore, considered that the sulphides may make a slight contribution toward the darkening of the quartz. The effect, however, appears to be a rather minor one unless the sulphides are extremely abundant. The same conclusions can be cited for the presence of tourmaline or other similar dark minerals.

Carbon and graphite have been proved to be present in the quartz from Yellowknife and other localities in the Precambrian of Canada, and since carbon and graphite absorb light strongly there is little difficulty in explaining the black or grey colour of the quartz. During the experiments it was noted that the colour varies from light grey to dark grey to black depending upon the quantity of carbon or graphite present in the quartz.

No special attempt was made in this investigation to determine whether or not small amounts of hydrocarbons were present in the samples. It may well be that a certain proportion of the black material in some black quartz is a hydrocarbon, but preliminary chemical experiments indicate that hydrocarbons are either rare or absent in the Yellowknife quartz.

It should be noted here that a distinction should be made between so called "smoky quartz," which is due to radioactivity or other electronic causes, and black or grey quartz due to other causes. The writer would restrict the term "smoky quartz" to quartz that can be proved to have derived its colour from radioactive or electronic processes, and the terms "black or grey quartz" to those varieties that owe their colour to some strongly absorbing impurity.

CONCLUSIONS

The black and grey quartz found in the veins and lenses of the Yellowknife greenstone and sedimentary areas owes its colour primarily to carbon or graphite distributed along planes or disseminated in the medium-grained quartz. Grey sulphides may serve to deepen the colour, but the effect is not notable unless the sulphides are present in large amounts. The variation in colour, grey to black, is a function of the amount of carbon or graphite present in the quartz.

A preliminary investigation of samples from other Canadian Precambrian areas suggests that carbon or graphite may be the most important colouring medium in grey and black quartz. Sulphides, tourmaline, and other dark minerals may be partly responsible for the dark colour of some quartz.

It is suggested that the term "smoky quartz" be restricted to the dark brown smoky variety that results from long exposure to radioactive emanations or other electronic causes, and that "black quartz and grey quartz" be applied to that variety which derives its dark colour from light absorbing impurities.

ACKNOWLEDGMENTS

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STUDIES OF MINERAL SULPHO-SALTS:
XVII—CANNIZZARITE

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Abstract

Cannizzarite, a lead, bismuth sulphosalt, from Vulcano, Lipari Islands, is redefined as a mineral species. Crystals are thin leafy blades, monoclinic, showing two lattices:

A; $P2/m$, $a=4.13$, $b=4.10$, $c=15.5$A, $\beta=99°00'$
B; $C2/m$, $a=7.07$, $b=4.10$, $c=15.5$A, $\beta=99°00'$

Hydrosynthetic experiments in the system Pb-Bi-S lead to the production of crystals of cannizzarite essentially similar to the natural material. Sufficient material, certainly free from bismuthinite and other Pb-Bi-S materials, was not available for quantitative chemical analysis.

Cannizzarite, occurring as a sublimation product in fumaroles on Vulcano, Lipari Islands, Italy was first described by Zambonini, de Fiore & Carobbi (1925). It is noted by Wolfe (1938) that Professor F. Bernauer found cannizzarite to be a mixture of bismuthinite and a platy, metallic mineral. Wolfe re-examined two specimens of cannizzarite from the type locality, available in the Harvard Mineralogical Museum collections. One, a bottle of loose acicular crystals, proved to be bismuthinite; minute, prismatic crystals from the second specimen yielded crystal measurements, structural cell dimensions, a new chemical analysis and a specific gravity which Wolfe ascribes to cannizzarite. Professor M. A. Peacock pointed out (Dana, 1944, 472) that these structural lattice dimensions and physical properties are identical with those reported for type galenobismutite by Berry (1940). Thus, in Dana, cannizzarite is reported to be identical with galenobismutite.

In the course of a study[2] of the synthesis of Pb-Bi-S compounds commenced at Queen's University in 1947 and continued at the University of Toronto in 1947–49 the first author synthesized, under hydrothermal conditions in a bomb, galena, galenobismutite and four other crystalline phases with probable compositions in the Pb-Bi-S system. One of these phases (Phase 2) gave an *x*-ray powder pattern identical with that given by thin leafy crystals from Wolfe's specimen of cannizzarite. This leafy material is probably the same as the platy mineral referred to by

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[1] Now with Dominion Gulf Company, 203 Bay Street, Toronto, Canada.

[2] Described fully in a thesis accepted for the degree Ph.D. *Synthesis and x-ray study of compounds in the systems Pb-Bi-S, Ag-Bi-S and Ag(Bi, Sb)S$_2$*, A. R. Graham, University of Toronto, 1950.

Professor Bernauer. The leafy material was exhausted in preparing the powder sample. In 1951 the latter authors examined a fine specimen of cannizzarite from the type locality which had been acquired from Ward's Natural Science Establishment by The University of British Columbia. A single leafy crystal from this specimen yielded rotation and Weissenberg *x*-ray films nearly identical with those given by the artificial crystals. This leafy mineral was apparently a component, along with galenobismutite and bismuthinite, of the material originally described as cannizzarite; therefore it is proposed that the old name be retained for this mineral. This present description is incomplete, lacking quantitative chemical data, but will serve to characterize the mineral as a crystalline phase in the system Pb-Bi-S and to ensure its future identification.

SYNTHESIS OF CANNIZZARITE

The methods of synthesis follow closely those used successfully by Robinson (1948) for compounds in the system Pb-Sb-S. This method utilizes a graphite-lined steel bomb fully described by Smith (1947) and Béland (1948). The details of charges and heating procedures for 30 experiments in the Pb-Bi-S system are given in Table 1. Crystals of phase 2 (=cannizzarite) were obtained in 8 experiments. In all cases phase 2 and artificial bismuthinite are intimately associated, but experiment 17 yielded the largest quantity of fairly pure material. The material occurs as felted masses, bundles of crystals loosely arranged in radial groups, and occasionally as stellate trillings made up of three doubly terminated individuals.

PHYSICAL PROPERTIES

The leafy blades are silvery grey and strongly striated parallel to their elongation. The individual crystals occasionally reached 2 mm. in length by $\frac{1}{4}$ to $\frac{1}{2}$ mm. in width, but they are extremely thin and fragile, twist and bend very easily and fray out at the ends and along their edges at the least touch. They appear friable rather than malleable but are difficult to crush to equidimensional fragments. The effects of preferred orientation in the powder sample are noticeable in the *x*-ray patterns.

Material from experiment 17 showed only traces of the bismuthinite pattern in powder photographs. Microchemical tests on clean crystals showed the presence of lead, bismuth and sulphur. Three specific gravity determinations, using a 10 cc. pycnometer and about 1.5 gms. of material give 6.64, 6.71, 6.75, average 6.7. The accuracy is not great because of the proven presence of bismuthinite (G (calc) 6.81).

Table 1. Hydrosynthetic Experiments in the System Pb-Bi-S

Exp.	$Na_2S \cdot 9H_2O$	S	H_2O	NaOH	Pb	Bi	Heated °C.	Heated Hours	Cooled to °C.	Cooled to Hours	Products
	g.	g.	g.	g.	g.	g.					
1	30	20	15	—	6	1	380	12	180	22	P, B, S, 1, N, L, H
									20	14	
2	30	20	15	—	4	2	400	12	180	9	P, B, S, 2, N, L, H
									20	12	
3	30	15	15	—	3	3	375	24	20	44	P, B, S, 3, N, L, H
4	30	20	15	—	2	4	410	26	210	72	P, B, S, 2, N, L, H
									20	12	
5	30	20	12	—	1	6	395	12	20	72	P, B, S, 3, N, L, H
					$PbCl_2$	$BiCl_3$					
6	25	15	17	—	1.8	9.3	395	24	190	36	P, B, S, 2, 4, N, L, H
									20	12	
7	20	10	20	—	2.7	6.0	405	30	260	60	P, B, S, 2, N, L, H
									20	24	
8	20	10	20	—	4.0	4.5	400	30	20	100	P, B, S, G, 2, N, L, H
9	20	10	20	—	5.4	3.0	400	30	20	48	
10	20	10	20	—	6	1.5	410	48	20	100	P, B, S, N, L, H
					Pb	Bi					
11	30	20	20	--	1	0.2	400	86	20	16	P, S, N, H
12	20	—	25	15	1	2	400	54	20	16	A, P, N, C
13	20	3	30	15	1	2					A, P, B, N, C
14	20	15	15	—	3	1					A, P, B, S, Ph, N, L, H
15	40	15	15	—	2	1					P, B, S, Ph, N, L, H
16	40	15	15	—	1	6					P, B, S, 2, N, L, H
				NaCl							
17	40	15	15	5	1	4					P, B, S, 2, N, L, H
18	40	15	15	5	1	3					P, B, S, N, L, H
19	35	15	15	5	1	3.5	400	54	20	8	P, B, S, N, L, H, C
20	35	15	15	2	1	5	450	32	40	7	P, B, S, N, L, H
21	35	15	15	2	1	5	400	54	chilled in air		P, B, S, N, L, H, C
22	35	15	15	2	1	7					
23	35	15	10	—	1	7					
24	35	15	15	—	1	8					
25	35	15	15	—	1	8	400	30	300	48	P, B, S, N, L, H, C
									220	3	
									quenched		
26	35	15	15	—	1	8	400	24	210	54	
									chilled in air		
27	35	20	10	—	1	20	400	6			
28	35	2	15	—	1	8			maintained at		A, B, N, C, and Bi
29	35	4	15	—	1	8			400 for 48 hrs.		oxide crystals
30	45	6	—	—	1	6			chilled in air		A, C

Abbreviations: A, Pb/Bi shot. P, PbS. 1, Phase 1. 2, Phase 2. 3, Phase 3. 4, Phase 4. B, Bi_2S_3. S, Sulphur. N, Soluble Na salt. H, Hydrogen sulphide. G, galenobismutite. Ph, pyrrhotite. L, yellow or brown oily liquid. C, black colloidal matter.

Note: Phases 1 and 4 are fine grained materials represented by certain x-ray powder lines in patterns of mixed materials. They could not be purified nor did they occur as single crystals.

The natural material from Vulcano (1927), Lipari Islands, consists of a single specimen about $1\frac{1}{2}\times 1\times 1$ in. in size. The porous lower portion of the specimen is composed of a dark substance intimately associated with a white granular powder which gave an *x*-ray powder pattern identical with that of apthitalite from Vesuvius. This material grades upward into a dark gray, fine-grained, vuggy rock with an irregular surface. Implanted on this surface and in the many vugs and cracks are small metallic lustred leaves which have a marked bluish to iridescent tarnish.

Under the binocular microscope, crystals with several different habits may be observed. Some are single straight laths with occasional frayed ends; some are twinned exhibiting a simple V shape; others composed of three blades show an open trigonal pyramidal shape; a few are triangular; and others occur as felted masses or loosely arranged stellate groups. All crystals are exceedingly thin and are often warped; many are striated parallel to their elongation. The individual crystals rarely reach 2 mm. in length by $\frac{1}{2}$ mm. in width; they are slightly elastic and are difficult to crush, suggesting that they are somewhat malleable.

Bismuthinite needles are present in small amounts.

STRUCTURAL LATTICE

Good signals were not observed on the optical goniometer from single terminated blades, but the crystals were readily oriented about their axes of elongation by using a strong train of signals from their striated surfaces. Rotation and zero and first-layer Weissenberg films about this axis using copper radiation showed the presence of two distinct lattices with the following characteristics.

Lattice A	Symmetry	a	b	c	β
Artificial	$P2/m$	4.09A	4.06A	15.39A	99°00′
Natural	$P2/m$	4.13	4.10	15.5	99°00′
Lattice B					
Artificial	$C2/m$	7.00	4.06	15.39	99°00′
Natural	$C2/m$	7.07	4.10	15.5	99°00′

The rotation axis is the monoclinic symmetry axis, b, for both lattices, and the period of this axis compares well with those of the elongation axis of a large number of mineral sulphosalts. The c-axis direction and period are also shared, the plane (001) is the plane of platy development in the crystals. The a axes of the two lattices, while coincident in direction have periods in the complex but rational ratio of 7 to 12. The zero and first layer of the reciprocal lattices, as plotted from the Weissenberg films are shown in Figure 1. The films from the artificial and natural crystals are essentially identical although the spots are large and

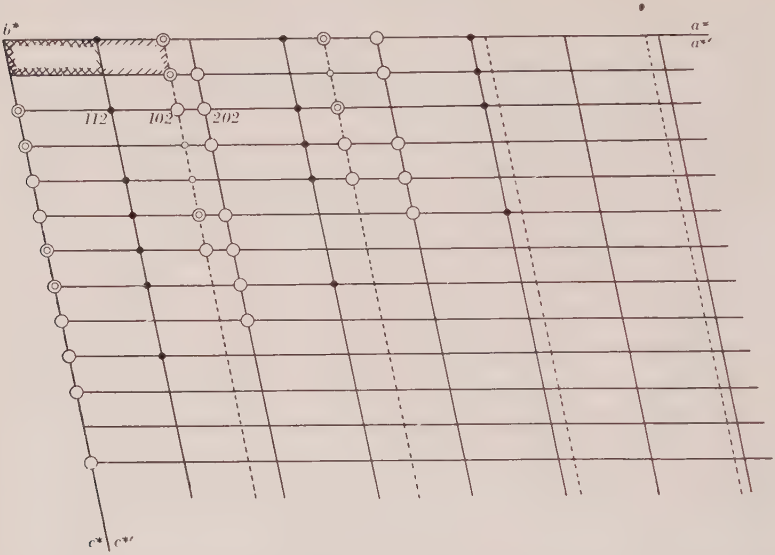

FIG. 1. Diagram of zero and first layers of the reciprocal lattice of phase 2 (=cannizzarite) plotted from Weissenberg photographs about the *b* axis. Large open circles are zero layer diffractions; small filled circles are first layer diffractions (of lattice B); small open circles represent maxima of smeared first layer diffractions (of lattice A).

generally diffuse on films from the natural material. On the films from artificial material all spots are sharp except for pronounced smearing in the 11*l*, 21*l*, and 31*l* festoons for lattice A on the first layer Weissenberg film. This suggests a partial disorder in the stacking of layers parallel to (001). This effect is not noticeable in a corresponding film from a natural crystal. Both lattices must be used to fully index the powder pattern measured on films from natural material given in Table 2.

The *x*-ray powder data given by Harcourt (1942) for "cannizzarite (=galenobismutite) from fumeroles, Lipari Islands, Italy H-89262" agree very closely with the data given in Table 2 for our natural material. These data are distinctly different from those for galenobismutite (Berry, 1940). Thus Harcourt's powder data (1942) represent the material described here as cannizzarite while Wolfe's crystal data (1938) refer to galenobismutite from the same locality.

The stellate trillings of artificial cannizzarite are due to the familiar twin law found in pseudo-hexagonal, monoclinic platy crystals. In such crystals when $b:a$ approaches $1:\sqrt{3}$ the angle $(100) \wedge (110)$ approaches 30° and twinning takes place on (110) as the twin axis with composition plane (001). In lattice B of these crystals, $b:a = \tan 30°07'$, twinning on (110) is therefore to be expected. Lattice A is evidently not responsible for the twinning.

TABLE 2. CANNIZZARITE—Pb, Bi, S—*X*-RAY POWDER DATA

Monoclinic—A: C_{2h}^1-P2/m; $a=4.09$, $b=4.06$, $c=15.39$, $\beta=99°00'$

B: C_{2h}^3-C2/m; $a=7.00$, $b=4.06$, $c=15.39$, $\beta=99°00'$

I	*θ*(Cu)	*d*(meas)	*hkl*	*d*(calc)	*I*	*θ*(Cu)	*d*(meas)	*hkl*	*d*(calc)
1	6.0°	7.38A	002	7.60	6	16.7°	2.68A	$\bar{1}$14B	2.68A
2	8.65	5.13	003	5.07				203B	2.67
10	11.65	3.82	$\bar{1}$02A	3.82	2	17.65	2.54	006	2.53
			004	3.80	½	18.8	2.39	$\bar{1}$15B	2.39
			101A	3.76	5	20.35	2.22	115B	2.21
3	12.75	3.49	110B	3.50				$\bar{1}$15A	2.21
			$\bar{2}$01B	3.49	5	22.35	2.03	$\bar{2}$01A	2.04
3	13.2	3.38	102A	3.36				$\bar{2}$02A	2.03
			111B	3.35				200A	2.02
			$\bar{2}$02B	3.35				$\bar{3}$12B	2.01
1	13.55	3.29	$\bar{1}$12B	3.28				$\bar{3}$11B	2.00
			201B	3.26	4	23.8	1.910	008	1.900
6	14.85	3.01	$\bar{1}$04A	3.01				312B	1.876
			$\bar{1}$13B	2.99	3	25.5	1.791	$\bar{1}$22A	1.793
			202B	2.98				121A	1.787
5	15.6	2.87	$\bar{1}$11A	2.87				313B	1.783
			110A	2.86	1	26.4	1.734	122A	1.737
2	16.2	2.76	$\bar{1}$12A	2.78				$\bar{2}$22B	1.736
			111A	2.76	2	27.25	1.684	025	1.688

I	*θ*(Cu)	*d*(meas)	*I*	*θ*(Cu)	*d*(meas)	*I*	*θ*(Cu)	*d*(meas)	*I*	*θ*(Cu)	*d*(meas)
½	28.45	1.618	1	31.2	1.488	1	35.55	1.326	1	38.75	1.232
1	29.35	1.573	½	32.35	1.441	1	36.55	1.295	½	39.95	1.201
½	30.35	1.526	1	33.85	1.384	½	37.25	1.274	2	41.15	1.172

The thin leafy character of cannizzarite and the constant association with bismuthinite and galenobismutite make the preparation of a suitable sample for quantitative analysis very difficult, and this has still to be done. The existing analyses were certainly made on mixed material and are therefore not representative of cannizzarite.

PHASE 3

This crystalline phase, designated here as phase 3 in the Pb-Bi-S system, possesses a powder pattern which found no exact counterpart in the patterns available from mineral specimens suspected of containing lead-bismuth sulphides. One powder pattern closely resembles that of phase 3; it represents a component of weibullite from Falun, Sweden, reproduced in Berry (1941). However the cell dimensions[1] given for this

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[1] Quoted in another paper appearing in this number, page 526.

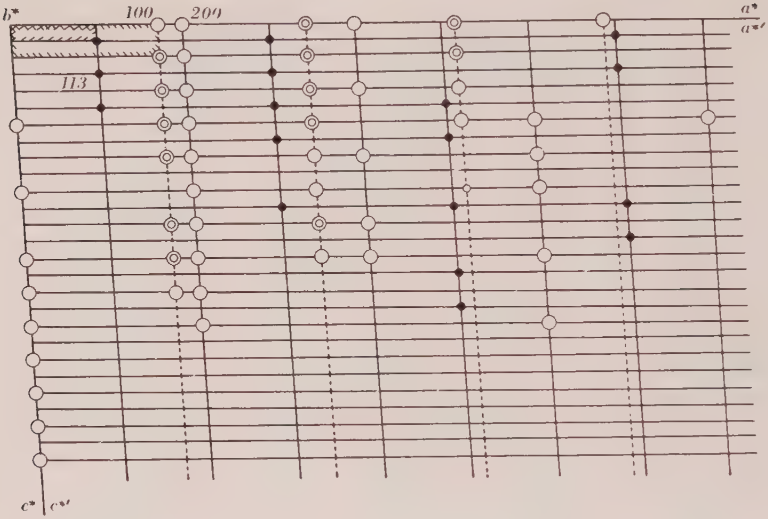

FIG. 2. Diagram of zero and first layers of the reciprocal lattice of phase 3 Pb-Bi-S system, plotted from Weissenberg photographs about the *b* axis. Large open circles are zero layer diffractions; small filled circles are first layer diffractions (of lattice B); small open circles represent maxima of smeared first layer diffractions (of Lattice A).

fibrous component of weibullite (Peacock & Berry, 1940, p. 68)—show very little similarity with those of phase 3 presented here.

Phase 3 resembles phase 2 (=cannizzarite) in habit; it occurs in typically thin, leafy crystals which bend easily and are so fragile that a touch causes fraying of the edges and splitting of the blades parallel to the lengthwise striations. As this habit is possible in bismuthinite, galenobismutite and cosalite, as well as in phase 2, only powder photographs can differentiate among the products of the experiments. The crystals reach about $1\frac{1}{2}$ mm. in maximum length, and a breadth of about $\frac{1}{4}$ mm.; they are extremely thin. No stellate trillings of phase 3 were observed although in individual habit and colour phase 2 and phase 3 are indistinguishable by inspection.

The crystals of phase 3 were sparser then phase 2, and insufficient could be obtained for tests requiring more than a few blades. Microchemical tests on clean blades were positive for lead, bismuth and sulphur, while no other elements were detected. The quantity of material was insufficient for specific gravity tests.

A single crystal was oriented to rotate about the elongation on the optical goniometer. Rotation and Weissenberg films about this axis show interpenetrating monoclinic lattices somewhat analogous to those of phase 2, with the following characteristics.

Lattice A:	$P2/m$	$a=4.11$,	$b=4.08$,	$c=18.58$A;	$\beta=93°35'$
Lattice B:	$F2/m$	$a=7.03$,	$b=4.08$,	$c=37.16$A;	$\beta=93°35'$

Like phase 2, phase 3 has the three axial directions in common, with equal periods for the rotation axis *b*, and the peculiar ratio of 7:12 for the lengths of the *a*-axis. Phase 3 differs from phase 2 in β-angle, in the *F*-centering of lattice B, and in the length of the *c* axes. The relationship of the A and B lattices of phase 3 is shown in Figure 2, a reciprocal lattice projection of the zero and first layer Weissenberg films. Smears on the first layer Weissenberg photograph show a condition of partial disorder in the stacking of the basal layers in lattice A. The disorder is more marked than in phase 2.

The observed intensities and spacings of the powder pattern lines are given in Table 3.

TABLE 3. PHASE 3—Pb-Bi-S—X-RAY POWDER DATA

Monoclinic, $A:P2/m$; $a=4.11$, $b=4.08$, $c=18.58$A, $\beta=93°35'$
$B:F2/m$; $a=7.03$, $b=4.08$, $c=37.16$A, $\beta=93°35'$

I	θ(Cu)	*d*(meas)	*hkl*	*d*(calc)	*I*	θ(Cu)	*d*(meas)	*hkl*	*d*(calc)
1	7.05°	6.32A	003A	6.18A	3	20.5°	2.20	1.1.13B	2.18
			006B	6.18	8	22.15	2.04	020A	2.04
10	11.85	3.75	012A	3.74				020B	2.04
			014B	3.74				$\bar{2}$02A	2.03
			005A	3.71				201A	2.02
			0.0.10B	3.71	1	24.3	1.873	024A	1.867
½	12.55	3.55	$\bar{1}$03A	3.52				028B	1.867
			200B	3.52				317B	1.862
3	13.2	3.38	113B	3.37				$\bar{3}$19B	1.862
			$\bar{2}$04B	3.36				0.0.10A	1.855
½	13.95	3.20	204B	3.22				0.0.20B	1.855
			$\bar{1}$04A	3.17	1	25.45	1.794	025A	1.787
7	14.9	3.00	$\bar{1}$17B	2.98				0.2.10B	1.787
			206B	2.97				$\bar{2}$13A	1.782
1	15.45	2.89	$\bar{2}$08B	2.92				$\bar{3}$.1.11B	1.780
			$\bar{1}$11A	2.89	½	26.15	1.749		
2	16.35	2.74	015A	2.74	½	27.05	1.698		
½	17.95	2.50	$\bar{1}$.1.11B	2.51	½	32.45	1.437		
			2.0.10B	2.47	½	33.95	1.380		
½	19.35	2.33	008A	2.32	½	35.55	1.326		
			0.0.16B	2.32	½	36.35	1.301		
			$\bar{1}$07A	2.29					

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NOTES AND NEWS

MINERAL OCCURRENCES IN WESTERN CANADA

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These notes describing some of the rarer ore minerals found during mineralographic studies, continue the series, the last of which appeared in *Am. Mineral.*, **36**, 504, 1951. I am pleased to acknowledge the assistance of Dr. H. V. Warren, A. R. Bullis, E. D. Dodson, J. A. Soles, and J. G. Souther, in collecting and/or examining ores.

Argyrodite. Ag_8GeS_6. Dolly Varden Mine, Alice Arm, Skeena M.D., B. C. This mine is located near the headwaters of the Kitsault River, 18 miles from the head of Alice Arm which extends northeasterly from Observatory Inlet. The mine has been inoperative for the past thirteen years but was well known during its brief history for its high silver values. A detailed discussion of the geology and mineralogy is given by Warren and Brown (*Trans. C.I.M.M.*, **45**, 1942, pp. 497–510).

The present discovery stems from a re-examination of some rich ore specimens by Mr. J. A. Soles, one of the writer's students in the course in mineralography. The samples examined consist of rather glassy bluish-black vuggy quartz containing pyrite and argentite. The ore minerals recognized under the microscope in approximate order of their abundance are: pyrite, argentite, galena, sphalerite, pyrargyrite, silver, chalcopyrite, tetrahedrite, polybasite, and argyrodite. The argyrodite was first thought to be tetrahedrite but it gave negative microchemical tests for copper. It was positively identified by comparing its *x*-ray powder pattern with that of argyrodite from type localities. The mineral has been found only in small amount in polished sections of ore from the 252 stope where it occurs with argentite in veinlets and fissures and appears to be closely associated with pyrite because it has not been observed in the more massive areas of argentite away from the strongly pyritized quartz. Until further work is done no generalizations as to its occurrence are warranted. It is interesting to note that silver minerals are associated with argyrodite at the type localities for this mineral, namely Saxony and Bolivia. In view of the present demand for germanium it would appear that silver deposits are good indicators of this element and should be closely studied. The writer has noted germanium in small amounts in spectrographic plates of coal ash, several sulphides, particularly sphalerite, and a few silicates, but can find no mention of a mineral containing essential germanium in North America.

Enargite. Cu_3AsS_4. Copper Mountain, near Castle Mountain Station on the Canadian Pacific Railway, Alberta. Copper Mountain is situated opposite the south end of Castle Mountain (now Eisenhower) across the Bow River. The area was prospected in 1884 and is described by Dawson (*Geol. Surv., Canada Ann. Report*, **135B,** 1886). Copper minerals are said to occur in quartz seams and lenses in Cambrian limestone.

The writer is indebted to Dr. W. H. Mathews for a specimen from this area. The small hand specimen examined consists of granular quartz stained with azurite and malachite and containing a 1 cm. patch of enargite on one corner. The mineral shows the typical cleavage and its identity was confirmed by an *x*-ray powder photograph. This occurrence is of interest as enargite has not been recorded previously in Canada.

In the University collections a sample labelled copper ore from Clearwater River east of Fort McMurray, Alberta, was found to be a solid cleavable mass of enargite with minor amounts of calcite and alteration rims of malachite. Unfortunately no information regarding its exact location or geological setting could be obtained.

Fergusonite. $(Y, Er, Ce, Fe)(Cb, Ta, Ti)O_4$. Tryagain Claim, Lemon Creek, Slocan M.D., B.C. Mr. D. Bain submitted a sample to the B. C. and Yukon Chamber of Mines for identification from his property located $2\frac{1}{4}$ miles above the Lemon Creek bridge on the Nelson-Nakusp highway. The sample, subsequently turned over to the writer, consists of a $1\frac{1}{2}\times 1\frac{1}{2}\times\frac{1}{4}$ inch mass of a brownish-black mineral with a subconchoidal fracture and a highly vitreous lustre. The hardness is 6 and the specific gravity 5.71. The mineral contains a small amount of admixed red feldspar. The mineral is in the metamict state but on ignition the structure was restored and an *x*-ray powder pattern in exact agreement with that of ignited fergusonite from Ytterby, Sweden, was obtained. The mineral gives a positive blowpipe test for uranium.

Lang (*Geol. Surv., Canada.* Paper 51-10, 46, 1951) reported allanite from the above locality. The only other known fergusonite locality in British Columbia is an occurrence 15 miles east of Kelowna (Lang, 46, 1951).

Gersdorffite. NiAsS. Mastodon Mine, near Revelstoke, Revelstoke M.D., B.C. Cubo-octahedral crystals of gersdorffite embedded in a groundmass of sphalerite and galena were observed in recent specimens received from this mine. The crystals are about $\frac{1}{2}$ mm. in size and give positive microchemical tests for nickel and arsenic but negative tests for cobalt. Their identity was confirmed by an *x*-ray powder photograph. Although cobaltite is a fairly common accessory mineral in several B. C. ores, the nickel analogue has not been recorded previously.

Matildite. $AgBiS_2$. How Group, Camsell River, N.W.T. The How Group is a part of the Camsell River Silver Mines' property and is located on the Camsell River about 20 miles south of Great Bear Lake.

The property is described by Kidd (*Geol. Surv., Canada* Memoir **187,** p. 33, 1936).

Dr. C. Riley, who was in charge of the development work on the property in 1935, kindly donated specimens which consist of a dolomite-quartz gangue with disseminated galena, chalcopyrite, pyrite, bismuth, and bismuthinite. Kidd (1936) noted that the bismuthinite was unusual in that it carried considerable silver.

One of the more interesting microscopic features of this ore is the fairly abundant galena-matildite exsolution intergrowth which exhibits a Widmanstätten texture. This intergrowth appears to be responsible for the majority of the silver content of the ore. Bismuthinite, usually contacting bismuth, occurs in small amounts. Associated with the above are sphalerite, chalcopyrite, traces of tetrahedrite, silver, argentite, marcasite, and minute zoned crystals of an undetermined iron cobalt nickel arsenic sulphide.

Owyheeite. $5PbS \cdot Ag_2S \cdot 3Sb_2S_3$. Rossland Mines Limited, near Rossland, Trail Creek M.D., B. C. Current development work on the Bluebird-Mayflower workings by Rossland Mines Limited makes a study of these ores of particular interest at the present time. The two workings are about 1000 feet apart on opposite sides of Gopher Creek, and are about $1\frac{1}{2}$ miles south of Rossland. A recent outline of the geology and development work is given by White (*Minist. of Mines B. C.*, Ann. Rept., 1949, 158).

A detailed mineralographic study of this ore was undertaken with a view to determining the nature and association of the silver, gold, lead, and zinc values. The several samples studied consist of a massive complex of sulphides and sulfosalts including pyrite, arsenopyrite, pyrrhotite, sphalerite, galena, and boulangerite as major constituents and minor amounts of tetrahedrite, owyheeite, meneghinite, chalcopyrite, and gold. Of particular interest is the occurrence of the owyheeite which appears to carry the main silver values. A fibrous, radiating, or interlocking mosaic of boulangerite crystals forms the groundmass of much of the ore. This encloses grains of pyrite, pyrrhotite, arsenopyrite, sphalerite, and galena either evenly disseminated or in irregular aggregates or crude bands.

Owyheeite, only recognizable under the microscope, is always intergrown with boulangerite, and under plane light the two minerals are difficult to distinguish. The owyheeite is slightly harder and less gray than the boulangerite. It has a rather yellowish cast. The yellow, blue, and purple polarization colours differ sufficiently from those of boulangerite to distinguish the two minerals under crossed nicols. The most satisfactory method of distinguishing these two minerals proved to be a 10 second etch with 1:1 HNO_3. The boulangerite is completely blackened in this time while the owyheeite is only slightly etched.

The galena contains laths of a slightly greenish-gray anisotropic mineral which proved to be meneghinite.

Owyheeite was first identified in two B. C. ores in 1948, and has since been reported from two other localities in British Columbia. In the absence of appreciable amounts of tetrahedrite or silver minerals, any silver bearing "jamesonite" should be regarded with suspicion.

Stannite. Cu_2FeSnS_4. Crowfoot Property, Magna Bay, Shuswap Lake, Kamloops M.D., B. C. Mr. S. Larder of Salmon Arm, B. C., submitted a suite of samples reputed to contain values in tin. Patches of stannite up to 1 cm. in size may be seen in a groundlmass of galena, sphalerite, pyrite, minor chalcopyrite and vuggy white quartz. Tin has not been reported previously in this area.

Tellurbismuth. Bi_2Te_3. Lucky Jim, Quadra Island, Nanaimo M.D., B. C. The presence of sylvanite at this property was suggested several years ago (*Minist. of Mines B. C.*, Ann. Rept., 1913, 286). Mr. J. Easton recently donated a sample of white quartz showing small platy masses of tellurbismuth intimately associated with gold.

Tetradymite. Bi_2TeS_2. Katanga Group, Pitt Lake, New Westminster M.D., B. C. This property is situated on the east side of Pitt Lake near the mouth of Scott Creek. The mineralization is reported to consist of pyrite and chalcopyrite which occurs in veins or dikes of a fine grained feldspathic rock up to 20 feet in width (*Minist. of Mines, B. C.*, Ann. Rept., 1930, 313).

Samples collected by Mr. G. A. Dirom consist mainly of massive arsenopyrite and minor chalocpyrite while one specimen shows coarse platy masses of tetradymite embedded in a groundmass of quartz, green diopside, and scheelite. This interesting association is evidently not typical of the mineralization.

Tetrahedrite (mercurian). $(Cu, Hg, Zn, Fe)_{12}(Sb, As)_4S_{13}$. Red Rock Group (formerly Brenda, *Minist. of Mines, B. C.*, Ann Rept., 1922, 187), near Skookumchuck, Fort Steele M.D., B. C. This property is situated on a small tributary of Skookumchuck Creek called Copper Creek about 6 miles west of Torrent Station. Samples reputedly from this property were presented to Dr. H. V. Warren through the kindness of Mr. N. Moe and consist of masses of tetrahedrite with minor pyrite in a quartz-siderite gangue. On close inspection of the material in the field, Dr. Warren noticed a few small red crystals in crevices and vugs in the tetrahedrite, and which were later identified in the laboratory as cinnabar.

A chemical analysis of the tetrahedrite was made by Mr. R. N. Williams on a sample with an average specific gravity of 4.95 and a cube edge of 10.3 A. A polished section of a portion of the material used for the analysis showed no impurities. The analysis is given on next page.

Cu	36.62
Hg	4.94
Zn	4.50
Fe	4.00
Sb	24.42
As	0.35
S	25.04
	99.87

A previous occurrence of mercurian tetrahedrite in British Columbia was described by Warren & Lord (*Econ. Geol.*, **30**, 67, 1935) from the Pretty Girl Claim of North Kootenay Mines Ltd., about 40 miles to the northwest of the Red Rock Group.

Wehrlite. Bi_2Te_3. Jones Creek, New Westminster M. D., B. C. This property variously known as the Laidlaw Group, Sovereign, and Telluride Gold Property, is situated a short distance above the Jones Creek bridge on the main highway about 12 miles west of Hope. Samples submitted from time to time consist of massive gold bearing arsenopyrite in quartz. Small quantities of wehrlite intimately associated with gold are occasionally seen embedded in quartz.

Monty Claim, Douglas Group, Clinton M.D., B. C. This claim is situated near the head of the North Fork of Watson Bar Creek. Highly weathered narrow quartz veins which contain less than two percent of oxidized pyrite show occasional small clean flakes of wehrlite. Crushed material yields numerous fine gold particles. Wehrlite was identified on a neighbouring claim (Ajax) in 1949.

AN OCCURRENCE OF URANINITE IN A BLACK SAND[1]

H. R. Steacy,[2] *Geological Survey of Canada, Ottawa, Canada.*

A sample of radioactive black sand reputedly taken from a placer deposit in British Columbia and submitted to the Geological Survey of Canada has been found to contain small amounts of uraninite. This occurrence is considered noteworthy because it is, so far as the writer has been able to learn, the first unquestionable identification of uraninite as a detrital mineral.

The sample submitted for examination is composed of the following minerals, listed in the order of their apparent abundance: magnetite (about 60 per cent by weight), hematite, garnet, chromite, pyrite, pyroxene, epidote, monazite, scheelite, native platinum, uraninite, cinnabar, and native gold.

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[1] Published by permission of the Director-General of Scientific Services, Department of Mines and Technical Surveys, Ottawa.

[2] Technical Officer, Geological Survey of Canada.

The uraninite occurs in blackish grains less than 0.2 millimeter in diameter. Most of the grains are rounded, and have a dull lustre, but a few are euhedral, showing excellent development of the cube and possessing an almost brilliant lustre. Identification was made from single grain *x*-ray diffraction photographs, *x*-ray fluorescence analyses, and qualitative chemical tests.

A further sample of the sand has been requested, from which it is hoped that a sufficient quantity of the mineral can be extracted for quantitative chemical analyses and, possibly, an age determination.

BENJAMINITE

E. W. Nuffield, *University of Toronto, Toronto, Canada.*

Benjaminite was originally described by Shannon (*U. S. Nat. Mus.*, Proc., **65,** art. 24, 1925) on specimens from the property of the Aikinite Mining Company near Round Mountain, Nye County, Nevada. The specimens had been collected and offered for study by a Mr. H. G. Clinton of Manhattan, Nevada. It was concluded from the name of the mining company that the material was aikinite and indeed it not only greatly resembled aikinite physically but gave the qualitative tests and polished section reactions for that mineral. However, Mr. Clinton later reported high silver assays from the material and Shannon confirmed the presence of this element by chemical tests. He derived the formula $Pb_2(Ag,Cu)_2Bi_4S_9$ from two partial and two complete chemical analyses and on this basis proposed a new mineral, benjaminite. Shannon reported that the mineral resembled massive tetrahedrite except that it showed a moderately good cleavage in one direction and that it was the only abundant metallic mineral in a quartz matrix. Associated minerals were muscovite, pyrite, molybdenite, chalcopyrite, fluorite and minor covellite and chalcocite.

I was fortunate to obtain the loan of Shannon's type material (U.S.N.M. 95058) from Dr. George Switzer and a Harvard specimen (HMM 85749) from Professor Clifford Frondel. Shannon's material consisted of a number of quartz-rich fragments, some of which had obviously supplied sections for Shannon's metallographic studies. The specimens closely resembled Shannon's description and I assumed that the abundant metallic mineral in the form of veins was the benjaminite. However it gave an *x*-ray powder photograph identical with that of aikinite ($PbCuBiS_3$) from Beresovsk. Subsequent investigation showed that all the material with the moderately good cleavage was aikinite and this constituted almost the whole of each vein. Thus Shannon's first impression was correct. It is likely that the cleavage and the silver

TABLE 1. BENJAMINITE: *X*-RAY POWDER DATA
$CuK_\alpha = 1.5418A$; Ni filtered

I	*d*(meas.)	*I*	*d*(meas.)	*I*	*d*(meas.)
7	3.47	6	2.00	½	1.453
½	3.18	1	1.943	½	1.410
½	2.95	½	1.845	2	1.322
10	2.82	3	1.752	2	1.271
1	2.18	1	1.705	1	1.157
½	2.07	2	1.633		

content influenced him to propose a new mineral. A cleavage was not attributed to aikinite in Dana (1892) and his polished section studies did not reveal the presence of a second, silver-bearing mineral.

Upon further examination of the material I noted a minute quantity of a second metallic mineral which gave an *x*-ray powder pattern distinct from that of known metallic minerals. This mineral occasionally showed a crystal face or cleavage on which a set of fine striations was just visible. A fragment was oriented on the Weissenberg goniometer to rotate about an axis in the plane of the crystal face and parallel to these striations. The rotation photograph yielded the lattice period 8.12A, but with a strong pseudo-period of 4.06A. The first layer proved too faint to resolve. However, resolutions of the zero and second layers were obtained which indicated a monoclinic pseudo-cell with dimensions a' 13.34, b' 4.06, c' 20.25A, $\beta = 104°$. The extinction conditions for this cell (*h*0*l* present with *h* even, *hkl* present with $h+k$ even) are characteristic for base-centering.

The material was insufficient in amount to attempt to obtain the usual physical and chemical data. It is probable however, that it is the mineral which contributed the Ag content to Clinton's assays and Shannon's analyses. It appears to be so sparse that close-sectioning would be necessary to intersect it and this probably accounts for Shannon's oversight. Although the name benjaminite was applied to a mixture of two minerals in which aikinite predominated it is reasonable to retain

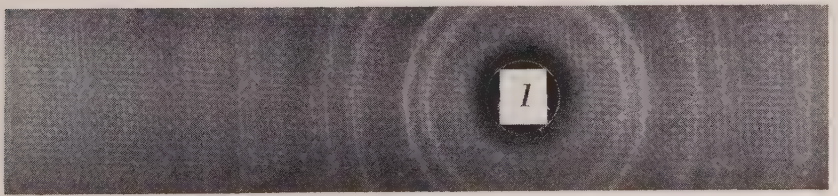

FIG. 1. *X*-ray powder photograph of benjaminite; Cu/Ni radiation, camera diameter 57.3 mm, actual size print.

the name for the Ag-bearing mineral which inspired his investigation. It is hoped that the powder data of Table 1 and the contact print of the powder pattern (Fig. 1) will result in locating sufficient material to permit a more complete description of this rare sulpho-salt.

A NOTE ON CONE AXIS AND UPPER LEVEL PRECESSION PHOTOGRAPHS

M. M. Qurashi[1] and W. H. Barnes,

Division of Physics, National Research Council, Ottawa, Canada.

I. *Accuracy of Parameters Obtained from Cone Axis Photographs*

In the determination of the unit cell constants of triclinic crystals with the Buerger precession camera, it is useful to be able to measure the d^* spacing normal to a particular zero-level plane with a reasonable degree of accuracy. Together with the shear obtained from the displacement of an upper-level net, this gives a complete description of a possible unit cell (*cf.* Buerger, *The Photography of the Reciprocal Lattice*, 1944; Fisher, *Am. Mineral.*, **37**, 1007–1054, 1952), which can then be transformed as desired. The direct determination of d^* from measurements of the diameters of the rings on a cone-axis photograph is not very accurate because (a) the crystal-to-film distance usually is known only approxi-

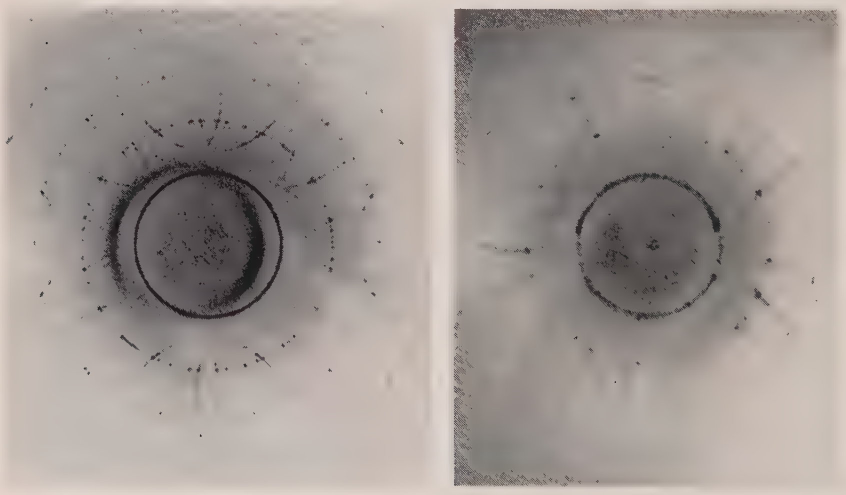
a b

FIG. 1. Cone axis photographs ($\mu = 20°00'$) of (a) pyrobelonite, (b) melanovanadite. (unfiltered Mo radiation)

mately, and (*b*) the film is rarely held perfectly flat in the layer-line screen holder.

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[1] National Research Laboratories Postdoctorate Fellow.

If the usual beam trap is used, the zero level is recorded on the film and serves as a calibration standard for the effective crystal-to-film distance, thus,

$$S_e = r_0/\tan \bar{\mu} \tag{1}$$

where $\bar{\mu}$ is the precession angle , and r_0 is the radius of the zero-level circle on the cone-axis photograph. This value of S_e can then be used to calculate $\bar{\nu}$ for the other circles recorded on the film. In this way an estimate of d^* accurate to 1% or better can be obtained. It is preferable to use unfiltered radiation to ensure that the zero-level ring will appear as a continuous circle, thus increasing the accuracy with which its radius can be measured.

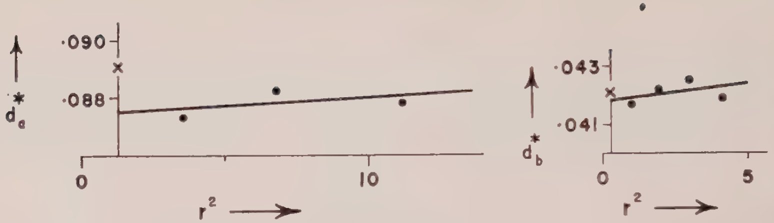
Fig. 1 shows cone-axis photographs of (*a*) pyrobelonite (orthorhombic) and (*b*) melanovanadite (triclinic) (Barnes & Quarashi, *Am. Mineral.*, **37,** 407–422, 1952). Two diameters for each circle were measured in the usual precession film measuring device; this is necessary because the traces of the levels frequently are markedly elliptical. The data for pyrobelonite are given in Table 1. It will be seen that the effective crystal-to-film distance (S_e) is about 5% greater than the nominal value of 30 mm. for which the layer-line screen, carrying the film, was set.

Table 1. Cone-Axis Data for Pyrobelonite ($\bar{\mu}=20°00'$)

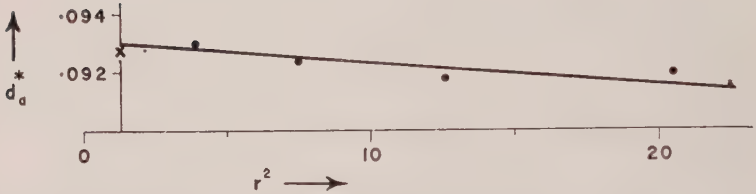
h	0	1	2	3	4
mean r_h (mm.)	11.48	19.82	27.40	35.48	45.28
	$S_e = r_0/\tan \bar{\mu} = 31.54$ mm.				
$\bar{\nu}$	20°00′	32°09′	40°59′	48°22′	55°08′
$\cos \bar{\nu}$	0.93969	0.84666	0.75490	0.66436	0.57167
hd_a^*	0	0.09303	0.18479	0.27533	0.36802
d_a^*	—	0.0930_3	0.0924_0	0.0917_8	0.0920_0
	mean $d_a^* = 0.0923 \pm 0.0003$				

The values of d_a^* are all within 1% of that (0.0927_6) obtained directly from the a^*b^* zero-level precession photograph. There is, however, some evidence of a systematic variation which probably is due to bulging of the film in the centre. Errors in d_a^* due to this cause will vary approximately as r_h^2 so that a more accurate value can be obtained by plotting d_a^* against r_h^2 and extrapolating linearly to r_0^2, for which S_e is known accurately.

Graphs of this type are shown in Fig. 2 for the two minerals. In the case of pyrobelonite, the extrapolated value of d_a^* is within 0.25% of



Melanovanadite



Pyrobelonite

FIG. 2. Graphs of d^* against r^2 for cone-axis photographs of pyrobelonite and melanovanadite; crosses at $r^2 = r_0^2$ indicate values of d^* obtained from 0-level precession films.

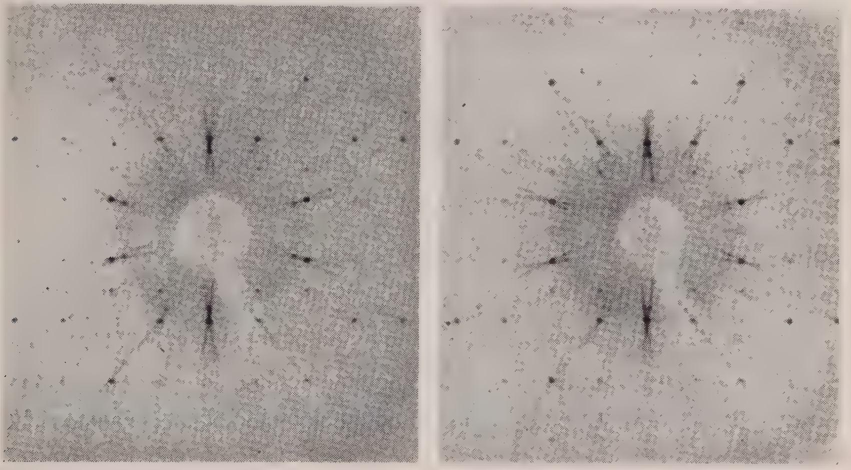
that obtained from the appropriate zero-level precession photograph and is most satisfactory. In the case of melanovanadite, however, the agreement between reciprocal spacings obtained from cone-axis and from precession photographs is not as good; 0.7% for d_b^* and 1.8% for d_a^*. The latter figure, however, represents the largest discrepancy observed among a number of such tests and is given to show that the method is useful even with crystals of poor quality. Those of melanovanadite usually occur as long needles with a helical twist about the needle axis.

In the foregoing discussion, the value of $\bar{\mu}$ is assumed to be exact. It is easily shown that the fractional error $\Delta d^*/d^*$ caused by an error $\Delta\bar{\mu}$ is less than $2\Delta\bar{\mu}/\bar{\mu}$. With the large vernier of the precession instrument, $\bar{\mu}$ is set readily to better than 0.05° so that this error will be well below 0.5% if $\bar{\mu} > 20°$. Film shrinkage errors, of course, are eliminated by the calibration and extrapolation procedure. Under favourable conditions, therefore, this method will yield values of d^* that are accurate to 0.5% or better. In fact, if an accuracy of only 2% or 3% is required, the diameters of the circles can be measured with a centimeter rule.

II. *Accurate Setting of the Cassette for Upper Level Photographs*

The increasing use of upper level precession photographs for intensity estimations is evident from the publication of charts for the appropriate L.p factors (Burbank, *Rev. Sci. Instr.*, **23,** 321-327, 1952; Grenville-Wells

& Abrahams, *Rev. Sci. Instr.*, **23,** 328–331, 1952). For such work it is desirable to obtain spots of a uniformly circular shape, which necessitates making *Fd** settings of the film cassette to better than 0.1 mm. Some methods of estimating and correcting errors in *Fd** are described by Buerger (*loc. cit.*).



a b

FIG. 3. First-level precession photographs of conichalcite, unfiltered Mo radiation, (*a*) setting error, $\Delta(Fd^*) = -0.3$ mm., (b) setting error, $\Delta(Fd^*) = +0.3$ mm.

For some time we have been using a somewhat different method which is both simple and effective. The basic principle is brought out in the photographs of Fig. 3, which were taken with unfiltered MoK radiation and for which *Fd** was intentionally misset by ±0.3 mm. It will be seen that the position of the cross-over of the two streaks of white radiation corresponding to each reflection is a function of the setting error; for perfect setting it should coincide with the position of the K_α reflection.

If the distance f between the K_α and K_β spots on either of the two streaks for a given reflection is measured, it can be used as a calibration standard, *viz.*, $(Fd^*)_\alpha - (Fd^*)_\beta \propto f$. Also, the error $\Delta(Fd^*) \propto f_1$, where f_1 is the distance of the crossover from either of the K_α spots that would coincide if there was no setting error. It follows that

$$f/f_1 = ((Fd^*)_\alpha - (Fd^*)_\beta)/\Delta(Fd^*) = (Fd^*)_\alpha(1 - \lambda_\beta/\lambda_\alpha)/\Delta(Fd^*)$$

whence,

$$\Delta(Fd^*) = (Fd^*)_\alpha(1 - \lambda_\beta/\lambda_\alpha)(f_1/f) \tag{2}$$

The direction of the required correction in *Fd** is evident from inspection of the photographs, *e.g.*, if the cross-over is between the K_α and K_β spots, the (*Fd**) setting is too small and must be increased.

Since $(1-\lambda_\beta/\lambda_\alpha)$ is approximately 0.1, even a rough estimate of (f_1/f) gives an accurate value of $\Delta(Fd^*)$. The accuracy can be estimated theoretically as follows.

From the geometry of upper-level precession recording and by an extension of Buerger's equation 29 (*loc. cit.*, p. 30),

$$_1 = \Delta(Fd^*) \tan \bar{\nu} + \Delta(Fd^*)\xi/d^*$$

so that,

$$f_1 = \Delta(Fd^*)\ (\tan \bar{\nu} + \xi/d^*) \tag{3}$$

An estimate of the probable value of ξ is required to evaluate this expression. Now, $\xi_{\text{min.}} = (\sin \bar{\nu} - \sin \bar{\mu})$, and $d^* = (\cos \bar{\mu} - \cos \bar{\nu})$, from which

$$F\xi_{\text{min.}} = Fd^* \cot ((\bar{\mu} + \bar{\nu})/2) \text{ cm.} \tag{4}$$

(if F is given in cm.). In view of the rapid decrease in intensity with increasing ξ, a reasonable average value for $F\xi$ is $(F\xi_{\text{min.}} + 2)$cm. Thus, by substitution in (3),

$$f_1/\Delta(Fd^*) \sim \tan \bar{\nu} + \cot ((\bar{\mu} + \bar{\nu})/2) + 2/Fd^* \tag{5}$$

and, therefore,

$$f_1/\Delta(Fd^*) \simeq 2.5 + 2/Fd^* \tag{6}$$

which is of the order of 4 or more for practical values of Fd^*. Consequently, if f_1 is measured to 0.5 mm., $\Delta(Fd^*)$ is known to about 0.1 mm. or better.[1] For comparison with Buerger's eq. 29,

$$f_B = \Delta(Fd^*) \tan \bar{\nu} \tag{7}$$

we obtain, from (3) and (7),

$$f_1/f_B = (1 + (\xi/d^*) \cot \bar{\nu}) \tag{8}$$

or, from (5) and (7),

$$f_1/f_B \sim (1 + (\cot ((\bar{\mu} + \bar{\nu})/2) \cot \bar{\nu} + (2/Fd^*) \cot \bar{\nu}) \sim 5 \text{ (or more} \tag{9}$$

The present method, therefore, is much more sensitive to ΔFd^* than one based solely on the linear displacement of the K_α spot.

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[1] For extreme accuracy, the white radiation streaks can be drawn on tracing paper by suitable manipulation of the precession film measuring device; f_1 and f can then be measured to within 0.1 mm.

THE SPACE GROUP OF CONICHALCITE

M. M. QURASHI[1] AND W. H. BARNES, *Division of Physics, National Research Council, Ottawa, Canada*, AND L. G. BERRY, *Queen's University, Kingston, Ontario, Canada.*

Conichalcite, $CaCu(AsO_4)(OH)$, is classified with the adelite group of minerals which is closely related to the descloizite group (*Dana's System of Mineralogy*, **2,** p. 804, 1951). The space group of descloizite, $ZnPb(VO_4)(OH)$, in the Dana orientation ($c<a<b$), generally is regarded as *Pnam* (Bannister, *Min. Mag.*, **23,** 376–386, 1933; Richmond, *Am. Mineral.*, **25,** 441–479, 1940), although for purposes of comparison with brackebuschite and pyrobelonite it is convenient to use the orientation $b<a<c$ for which the corresponding space group notation is *Pnma* (Barnes & Qurashi, *Am. Mineral.*, **37,** 407–422, 1952). This orientation also has the advantage from the *x*-ray crystallographic point of view that it is the standard form for D_{2h}^{16} (*International Tables for X-Ray Crystallography*, **1,** 151, 1952). The space group of adelite, $CaMg(AsO_4)$-(OH,F), is reported to be $P2_12_12_1$ (Hägele, *Neues Jahrb. Min.* Abt. A, Beil.-Bd. 75, 101, 1939), with only very weak reflections eliminating the *n* and *a* glides. From this fact, and the general similarity of the reflection intensities from the principal zones of both minerals, Hägele argues that the space group of descloizite also is $P2_12_12_1$ but that the *hk*0 reflections for which *h* is odd, and the 0*kl* reflections for which $k+l$ is odd, are too weak to be observed. This, in turn, suggests that the space group of conichalcite probably is $P2_12_12_1$, as conjectured in Dana (*System of Mineralogy*, **2,** p. 806).

X-ray studies of conichalcite, however, have produced two different space group assignments, *Pmma* (for "higginsite," Richmond, *Am. Mineral.*, **25,** 441–479, 1940) and *Pnma* (Berry, *Am. Mineral.*, **36,** 484–486, 1951) after interchanging *b* and *c* in each case, both of which have $P2_12_12_1$ as a possible lower symmetry.

We have now examined crystals from two localities as follows:

(*a*) "higginsite" type material from the Higgins Mine, Arizona (Harvard Museum, 92923), of which two different fragments, cut from separate, small, crystals, gave identical results.

(*b*) material labelled "erinite" from Tintic, Utah (Royal Ontario Museum, E3001) and identified by powder and Weissenberg methods as conichalcite (Berry, *Am. Mineral.*, **36,** 484–486, 1951).

Zero level precession photographs for the 0*kl* zone are shown in Fig. 1 for the two types of material, (*a*) and (*b*), and it will be observed that several reflections for which $k+l$ is odd are clearly visible. In fact, spots

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[1] National Research Laboratories Postdoctorate Fellow.

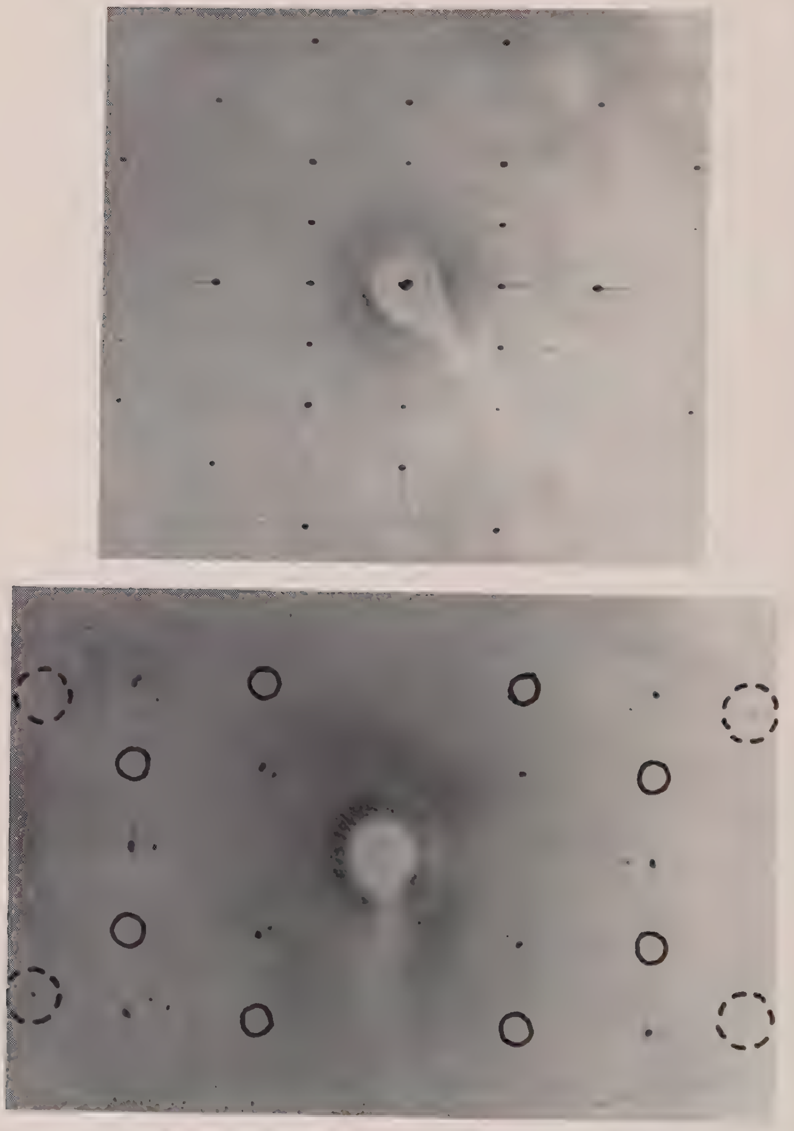

FIG. 1. Conichalcite; zero level, a axis, precession photographs, b^* horizontal, c^* vertical. Top "higginsite", filtered MoK_α radiation. Bottom "erinite", unfiltered Fe radiation; K_α spots, {012}, {021}, indicated by circles, K_β spots, {032}, indicated by dotted circles.

due to the following reflections are present in the original negatives: 012; 021; 032, 034; 036, 038; 052, 054, where the indices refer to the *Pnma* orientation. Reflections, in the *hk*0 zone, for which *h* is odd are considerably weaker, and the corresponding precession photographs are not suitable for reproduction. The following reflections, however, have been observed: 120, 140; 310; 360; 530, 550; 710, 730, 740. Precession photographs, therefore, show only axial halvings for the principal zones, and there are no systematic *hkl* absences, so that the space group of conichalcite is now established as $P2_12_12_1$. It is interesting to note that the list of observed reflections that forbid the *n* and *a* glides in conichalcite is very similar to corresponding observations on adelite (Hägele, *Neues Jahrb.* Min. Abt. A, Beil.-Bd. 75, 101, 1939). It may also be pointed out that the case of conichalcite serves as another example of the power of the Buerger precession method for space group investigations.

The structure of conichalcite is under investigation in connection with studies of the minerals of the descloizite group at the National Research Laboratories. It is appropriate, therefore, to mention at this time that a few very weak spots corresponding to reflections with $k+l$ odd have now been observed on a 200-hour 0*kl* Weissenberg film of descloizite. Thus it appears that Hägele's contention that the space group of descloizite is $P2_12_12_1$ probably will be confirmed. If so, then the necessity for separating the adelite and descloizite groups, at least on structural grounds, would virtually be eliminated. This will be discussed in greater detail in connection with the structure determination at present in progress on conichalcite, descloizite, pyrobelonite, and brackebuschite.

COMPLEX INCLUSIONS IN PEGMATITIC MINERALS

F. G. Smith, *University of Toronto, Toronto, Canada.*

Recently I reviewed the literature on mineral inclusions and related facts which have a bearing on temperature of crystallization. It was surprising to find a considerable amount of excellent descriptive and illustrative data in petrographic and mineralogic papers published throughout the last century. It was even more surprising to note that the early workers, such as Brewster, Sorby, and Zirkel observed many features of inclusions which are not mentioned in most current works. The question arises: were the earlier observations erroneous or are the current workers failing to notice these features?

It has been recorded that certain pegmatitic minerals contain complex inclusions which consist of intergrowths of minute crystals, usually with one or more liquids, and often one or more gas bubbles as well.[1] It was postulated in the past, and it still seems reasonable, that such inclusions represent small specimens of silicate liquid present when the minerals originally were formed or when the minerals subsequently were cracked and healed, or recrystallized. However, a number of recent studies of inclusions in pegmatite minerals have shown the absence of this type of inclusion and the abundance of fluid inclusions containing liquid water (with or without carbon dioxide) and a vapor bubble. A reconnaissance examination of pegmatitic minerals by the writer has confirmed this generalization, but in two specimens of idiomorphic quartz, the complex multi-crystalline inclusions were seen, and the only normal fluid inclusion were in a few secondary planes.

The above facts suggest the following hypothesis: the crystallization of at least the early pegmatitic minerals was in the presence of a hydrous silicate liquid, which became included in small amount in the minerals and crystallized there, but subsequently the pegmatite itself was crushed, healed, recrystallized, and/or decomposed by hydrothermal solutions, which left secondary inclusions in some of the minerals. A test of this hypothesis would consist of an examination of uncrushed pegmatitic minerals, which may occur only in drusy cavities. It is significant that most of the early data on complex multi-crystalline inclusions was obtained in the study of gems, which contain few or no planes of secondary inclusions.

In other words, I am suggesting that most of the liquid inclusions in pegmatitic minerals are of secondary (=subsequent) origin and the composition of such inclusions may bear no simple relation to the composition of the liquid present during the first crystallization. Only the inclusions in crystals which grew in druses or otherwise were protected from later fracturing can be used to deduce the character of the solutions which deposited the crystals.

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[1] Bilgram, H.: *Proc. Acad. Nat. Sci., Phil.*, **55,** 700, 1903. Brewster, D.: *Trans. Roy. Soc. Edinb.*, **10,** 1–14, 1826; *Idem*, **16,** 11–22, 1845; *Phil. Mag.*, **33,** 489–493, 1848; *Idem* (4), **5,** 235–236, 1853; *Trans. Roy. Soc. Edinb.*, **23,** 39–44, 1861. Currie, J. B.: *Econ. Geol.*, **46,** 765–778, 1951. La Vallée Poussin, C. de, & Renard, A.: *Mem. Cour. Acad. Roy. Brux.*, **40,** 34–45, 1876. Lindgren, W.: *U.S.G.S., Prof. Paper* **43,** 213–218, 1905. McMahon, C. A.: *Br. Assoc. Adv. Sci.*, 589–596, 1902. Prinz, W.: *Bull. Soc. Belge Micr.*, **8,** 97–105, 1882. Smith, F. G.: *Am. Mineral.*, **37,** 470–491, 1952. Sorby, H. C.: *Phil. Mag.* (4), **15,** 152–154, 1857; *Quart. J. Geol. Soc. London*, **14,** 453–500, 1858. Sorby, H. C., & Butler, P. J.: *Proc. Roy. Soc. London*, **27,** 291–302, 1869. Zirkel, F.: *Sitz. Akad. Wiss., Math.-Natur. Cl.*, **47,** 226–270, 1863; *N. Jahrb. Min.*, 769–787, 1866; *Die mikroskopische Beschaffenheit der Mineralien und Gesteine*, 39–85, 149–150, 1873; *Prof. Papers Eng. Dept., U. S. Army* (18), **6,** 1–297, 1876.

WALKER MINERALOGICAL CLUB*

OFFICERS 1952

Honorary President, A. L. Parsons; *President,* J. A. MacDonald; *Secretary-Treasurer,* Mrs. Helen Bush; *Editor,* L. G. Berry; *Councillors,* C. L. Coleman, R. Ford, D. Hogarth, V. B. Meen, G. G. Waite.

ABSTRACT OF PROCEEDINGS, 1952

January 31, 1952. The Walker Mineralogical Club met in the Royal Ontario Museum of Geology and Mineralogy. Mr. W. A. Tovell, lecturer in the Geological Sciences, University of Toronto, described the new plan for the Geological galleries. Dr. V. B. Meen, Director of the Royal Ontario Museum of Geology and Mineralogy, outlined briefly the arrangment of the cases in the gallery of Mineralogy. Minerals donated to the club by Mr. C. B. Gerber, Arlington, Va. were distributed to members. Refreshments were served.

February 28, 1952. The financial statement for the year 1951 was presented by the Secretary-Treasurer—Balance on hand in Ordinary Account—$409.50; Balance on hand in Prize Fund Account—$105.17; Bonds for Prize Fund Account held in safekeeping—$900. Dr. G. B. Langford, Head of the Department of Geological Sciences, University of Toronto, addressed the Club on the subject "Mineral Economics," and illustrated his talk with slides.

March 26, 1952. Dr. G. Switzer, Associate Curator, Department of Geology, United States Natural Museum, Washington, D. C., spoke to the club on "Collecting Aquamarines in the Colorado Rockies." Slides illustrated his address.

May 1, 1952. Dr. V. B. Meen was chairman for a programme entitled "The Hows and Whys of Mineral Collecting." G. G. Waite as an "oldtimer" and Miss Ruth Jenking as a "newcomer" gave brief talks; V. B. Meen spoke on "Mineral Occurrences and Associations"; G. Steel discussed collecting operations and equipment; F. Ebbutt dwelt on preparation, labelling, packing and display of specimens; C. C. Stevenson dealt with trading and where to buy minerals; V. B. Meen completed the programme with a brief history of the club.

May 17, 1952. Members gathered at the Forks of the Credit, Ontario to hunt orange celestite.

October 10–13, 1952. The Sixth Annual Field Trip was held at Bancroft, Ontario. The following localities were visited—McDonald Quarry, Woodcox Quarry, Bird Creek, Goulding Keene Nepheline Quarry, York River Quarries, Princess Quarry, Fission Property and Clark's Fluorspar Property near Wilberforce, Graphite Mine at Harcourt, Emily Mine and Marble Quarry at Madoc. A square dance was held Saturday night while slides of former field trips were shown on Sunday night.

November 13, 1952. The Club met at the Lighting Institute where Mr. J. A. Bateman, Manager of the Lighting Institute, Canadian General Electric Company, addressed the members on "Light and Ultra-Violet Radiation." Demonstrations were held. A gift of fluorescent minerals, presented to the Club of E. J. Tolamini, Kearny, N. J., was distributed. Refreshments were served courtesy of the Lighting Institute.

December 11, 1952. Elections of officers for 1953 were held. The President announced that F. Ebbutt, M. H. Frohberg, G. Steel and G. Waite had been honoured by being made life members of the Royal Ontario Museum of Geology and Mineralogy. It was also announced that the Peacock Memorial Prize for 1952 had been awarded to R. J. Traill, Geological Sciences, Queen's University, Kingston, Ontario, for his paper entitled "Synthesis and X-Ray Study of Uranium Sulphate Minerals." Mr. F. Ebbutt, geologist for Howe Sound Explorations Co., spoke on "Spanish Exploration and Mining in Mexico." Slides were shown.

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* Founded in 1938 and named in honour of the late Professor T. L. Walker (1867–1942), then Professor Emeritus of Mineralogy and Petrography in the University of Toronto and Director of the Royal Ontario Museum of Mineralogy. The by-laws of the Club were published in *Am. Mineral.*, **34,** 469, 1949.

The Peacock Memorial Prize of One Hundred Dollars Cash is offered by the Club for the best scientific paper on pure or applied mineralogy. A full announcement of the conditions governing the award appeared in the March–April 1953 issue of *The American Mineralogist.* The papers must reach the secretary, Walker Mineralogical Club, 100 Queen's Park, Toronto, not later than June 30, 1953.

The Council of the Walker Mineralogical Club wishes to acknowledge the courtesy of the Council of the Mineralogical Society of America in again making possible the publication of a Canadian number of *The American Mineralogist.*

MRS. HELEN BUSH, *Secretary-Treasurer*

ANNUAL MEETING

The thirty-fourth annual meeting of the mineralogical Society of America will be held in Toronto, Canada, Monday through Wednesday, November 9–11, 1953. A series of field trips is being planned for Thursday, Friday and Saturday following the meeting.

Abstracts of papers to be presented at the annual meeting must be received by the Secretary on or before *July 15, 1953.* Abstract blanks may be obtained from the Secretary.

NOMINATIONS OF OFFICERS FOR 1954

President: Sterling B. Hendricks, U. S. Department of Agriculture, Beltsville, Maryland

Vice-President: Harry H. Hess, Princeton University, Princeton, New Jersey

Secretary: C. S. Hurlbut, Jr., Harvard University, Cambridge, Massachusetts

Treasurer: Earl Ingerson, U. S. Geological Survey, Washington, D. C.

Editor: Walter F. Hunt: University of Michigan, Ann Arbor, Michigan

Councilor (1954–57): Felix Chayes, Geophysical Laboratory, Washington, D. C.

The above Fellows have been nominated by the Council as officers of the Mineralogical Society of America for 1954. They will be voted on at the election in October 1953.

C. S. HURLBUT, JR., *Secretary*